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13. ABSTRACT (Maximum 200 Words)
By utilizing both the Heck and Wittig reaction, an orthogonal approach was developed towards the stepwise synthesis of end-functionalized oligo-phenylenevinylenes. A significant advantage of this approach is that no protecting group chemistry is involved and this approach can be further utilized to synthesize dendritic molecules with PPV structures. The funtionalized OPVs can be further coupled with other functional polymers to form diblock copolymers. These OPV exhibit liquid crystallinity and luminescent properties.

Recently, a new photorefractive polymer which contains an ionic tri(bispyridyl) ruthenium complex as the charge generation species, a conjugated polymer backbone as the charge transporting channel and a nonlinear optical chromophore was designed and synthesized. These polymers designed to address numerous issues still unresolved in photorefractive polymer systems. A crucial one is associated with the photoconducting process, that is, both the low quantum yield of the photogeneration of charge carriers and the low mobility of the charge carriers. The ruthenium complex was introduced to utilize its efficient light induced metal-to-ligand charge transfer process. This polymer shows greatly enhanced photorefractive performance; a large net optical gain of about 300 cm-1 was obtained at a zero external electric field.

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1.   W. J. Li, T. Maddux and L. P. Yu, "Synthesis and Characterization of Diblock Copolymers Containing Oligothiophenes With Defined Regiospecificity and Molecular Weights", *Polym. Preprints, 37(2)* , 378 (1996).

2.   W. J. Li, T. Maddux, L. P. Yu, "Syntheses of Oligothiophene with Defined Regiospecificity and Molecular Weights and Its Diblock Copolymers", *Macromolecules, 29*, 7329, (1996).

3.   T. Maddux, W. J. Li and L. P. Yu, "Stepwise Synthesis of Substituted Oligo(phenylene-vinylene) via an Orthogonal Approach", *J. Am. Chem. Soc.,119*, 844, (1997).

4.   S. Deb; T. Maddux and L. P. Yu, "A Simple Orthogonal Approach to Polyphenylenevinylene Dendrimers", *J. Am. Chem. Soc., 119*, 9079, (1997).

5.   W. J. Li, T. Maddux, L. P. Yu, "Stepwise Synthesis of Substituted Oligo(phenylene-vinylene) via an Orthogonal Approach and Their Diblock Copolymers", Submitted to *Macromolecules*.

A. Synthesis and Characterization of Photorefractive Polymers Containing Transition Metal Complexes as Photosensitizer.

Photorefractive effect involves the modulation of the index of refraction of a material by a space charge field via the electro-optic effect.[2] This space charge field arises from the redistribution of charges in a photoconductor when it is illuminated with a nonuniform light intensity pattern. Since the change of refractive index is proportional to the magnitude of the space charge field, the generation of a large space charge field is crucial for a high PR performance. The formation of a space charge field involves three processes: the generation of free charge carriers, the transport of them and eventually trapping by a trapping center. Therefore, in order to build up a large space charge field, the optimization of these three processes is essential.

In the majority of these inorganic ferroelectrics ($BaTiO_3$, $Bi_{12}SiO_{20}$ (BSO), $Sr_xBa_{1-x}NbO_3$ etc.) with a pronounced photorefractive effect, Fe^{2+}/Fe^{3+} impurities play the most important role as electron donor and trapping centers. It is believed that the photoinduced

interconversion of $Fe^{2+} <-> Fe^{3+}$ and the efficient band transporting of the free charge carriers are responsible for the buildup of space charge fields.

Unlike their inorganic counterpart, organic PR materials lack such mechanisms for the formation of the photoinduced space charge field.[1(a)] Their photogeneration of charge carrier is accomplished through exciton dissociation and free charge carriers are transported away through a hoping mechanism along a series of transporting molecules. Because of the low dielectric constant and numerous channels for the relaxation of excited states to the ground state, the quantum yield for the charge generation in organic materials is usually low. To address these problems, we recently designed a new photorefractive polymer system which contains multivalent transition metal complexes (Ru^{2+} or Os^{+2} complexes) and conjugated polymer backbones. In this system, the conjugated polymer backbone was chosen to play the dual role of both transporting channel for the charge carriers and the macroligand to chelate with the transition metal-complex.

It is well known that doped conjugated polymer systems have high electrical conductivities.[5] Although band transport theory may not be valid for the charge transporting in these systems. Charge transporting through polaron or bipolaron states which are resided in the forbidden gap could be also very efficient.[6] Therefore, conjugated backbone could provide an efficient charge transporting pathway and it could facilitate the formation of the space charge field. Ru(II)-tri(bispyridyl) complexes were chosen as the photocharge generator. $Ru(bpy)_3^{2+}$ is known to exhibit interesting metal-to-ligand charge transfer (MLCT) process and have been extensively studied on their behavior in photochemistry, photophysics, electrochemistry, and electronic/energy transfer process.[7] They have also been extensively studied as light-harvesting materials, materials which can reduce water into hydrogen when coupled with other components.[8] To utilize their interesting charge transfer properties in the synthesis of PR polymers, Ru(II) complexes were designed to chelate with the conjugated polymer backbone. Upon excitation in the region of the MLCT transition of the Ru complex, electrons would be injected into the polymer backbone (equivalent to n-doping of PPV), transported away through either intrachain migration or

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interchain hopping and eventually trapped by the trapping centers which could be impurities or structural defects. We envision that the combination of the efficient MLCT process of the ruthenium complexes and the efficient charge transporting process of the conjugated backbone will lead to a higher charge separation efficiency and therefore better PR performance in this new PR polymer system. Experimental results confirmed that the incorporation of the Ru-complex into the PR polymers indeed dramatically enhanced the PR performances of the resulting polymers. This approach is versatile and has been extended to synthesize Os-complex containing PR polymers which showed photorefractivity at a wavelength in the near IR regions.

A-1. Since the targeted polymer is a multifunctional polymer which contains conjugated system, NLO chromophore and ionic transition metal complex, a reaction which can tolerate all of these functionalities and possesses high yield should be utilized for the polymerization. From our previous studies and other groups' works, the Heck coupling reaction is found to be versatile to synthesize conjugated polymers.[9] Its mild reaction condition and tolerance for a variety of functional groups are especially useful for synthesizing such functional polymers. We have previously demonstrated that the Heck coupling reaction can be utilized to synthesize conjugated polymers containing ionic transition metal complexes and the resulting polymer showed enhanced photoconductivity.[10] That work is the bases for the design of our new PR polymers.

Synthesis of the monomers and polymers: To utilize the Heck reaction, Ru-complexes bearing diiodofunctional groups were synthesized according to Scheme 1 where the 5,5'-dimethyl 2, 2'-bipyridine was synthesized by the Raney nickel catalyzed self-coupling of 3-picolines. Compound **6**, a crucial compound for this approach, was synthesized by reacting compound **5** with 1 eq. butyllithium and subsequent quenching by DMF. The Horner-Wittig-Emmons (HWE) reaction between compounds **3** and **6** yielded compound **7**. The final ruthenium (or Osmium) complex (monomers **A** or **B**), soluble in common organic solvents, was prepared after refluxing the compound **7** with Ru(bipy)$_2$Cl$_2$ (or Os(bipy)$_2$Cl$_2$) and can be easily purified by recrystalization from THF/Hexane.

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Scheme 1. Synthesis of the Ru(or Os)-complex (monomers **A** and **B**).

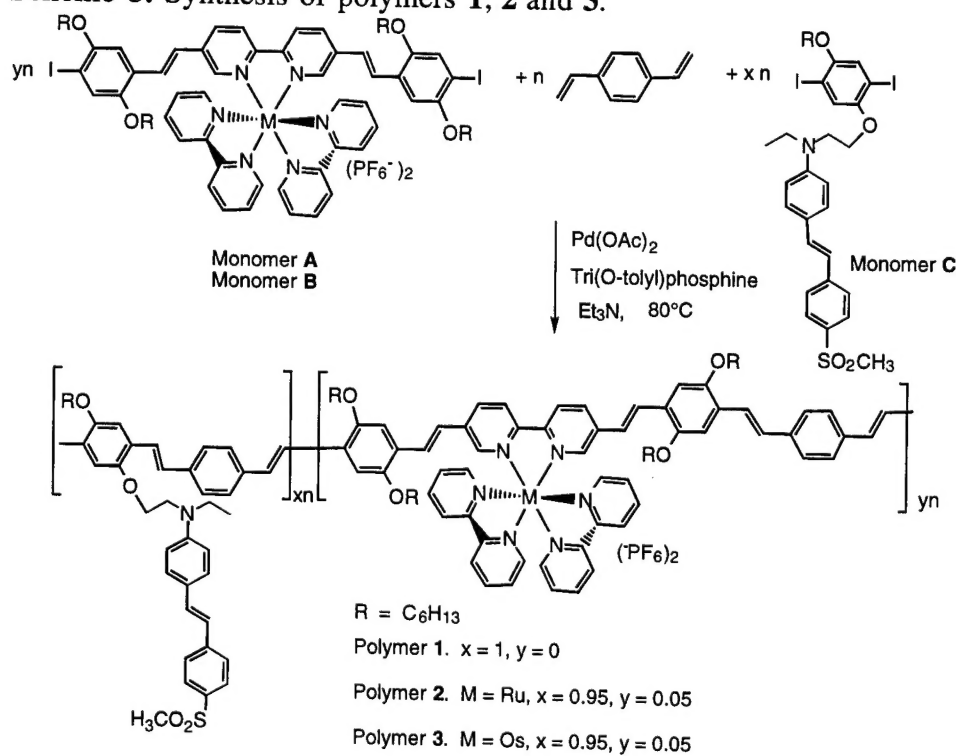Monomer **A**: **M = Ru.**
Monomer **B**: **M = Os.**
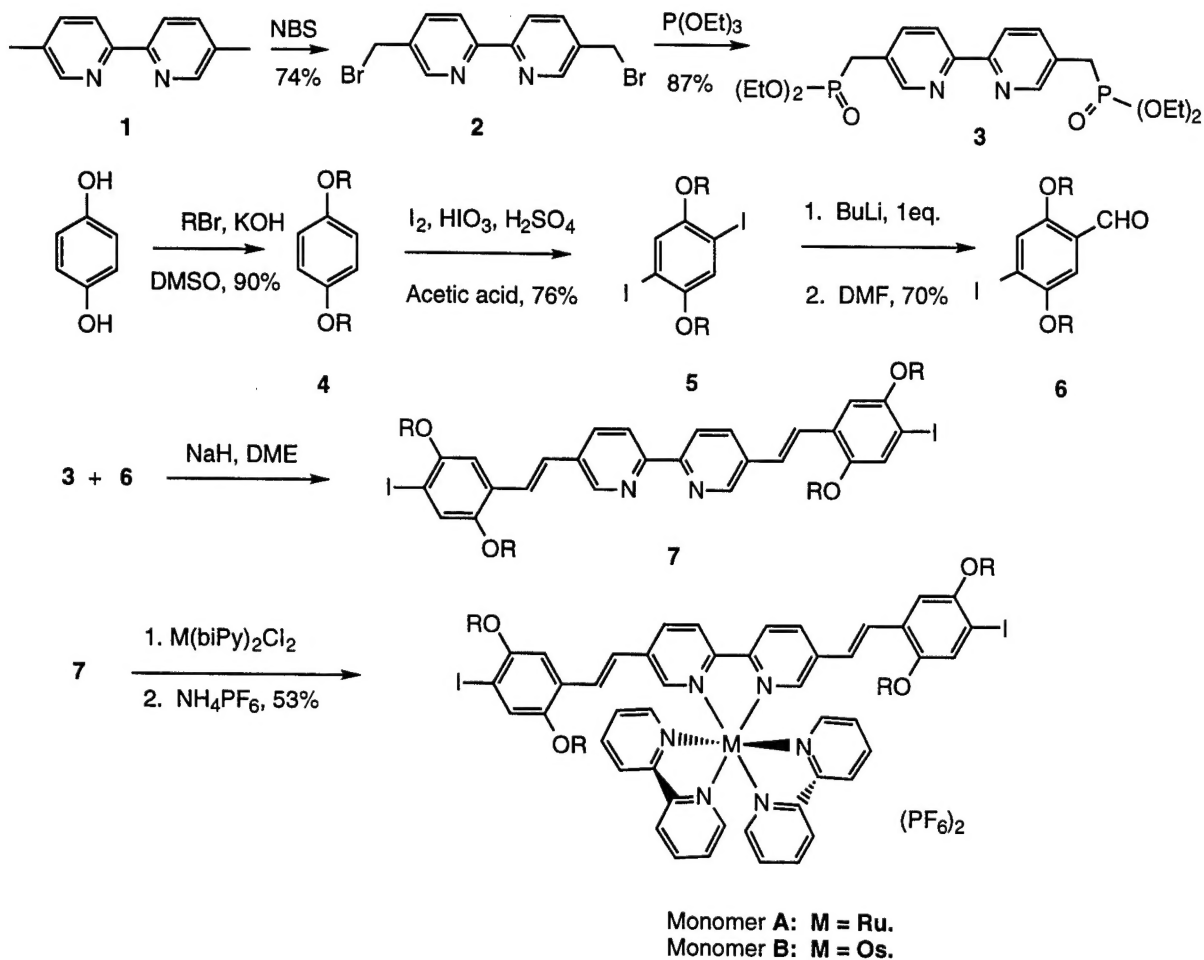
Monomer **C** was synthesized by using the approach outlined in Scheme 2. This monomer contains an alkoxyl substitutent which was introduced to increase the solubility of the resulted conjugated polymers; the polymer without this substitutent was insoluble in common organic solvents due to the strong interchain π-π interactions.

Scheme 2. Synthesis of monomer **B**.
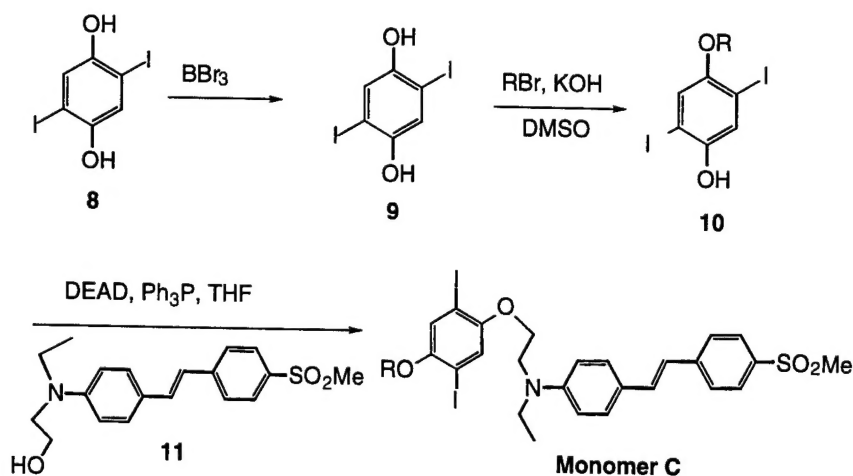
The polymerization was carried out according to Scheme 3 where the Pd(OAc)$_2$/P(o-tolyl)$_3$/NEt$_3$ (0.04 : 0.2 : 2.5 mol ratio relative to divinyl benzene) was applied as the catalytic systems. Polymers soluble in tetrachloroethane, DMF, NMP were obtained in excellent yields.

Scheme 3. Synthesis of polymers **1**, **2** and **3**.

R = C$_6$H$_{13}$

Polymer 1. x = 1, y = 0

Polymer 2. M = Ru, x = 0.95, y = 0.05

Polymer 3. M = Os, x = 0.95, y = 0.05

Structural characterization: Polymers **1** and **2** are insoluble in THF, chloroform but soluble in tetrachloroethane (TCE), DMF, NMP etc. Their intrinsic viscosities were measured to be 0.46, and 0.53 dL/g, respectively, in NMP at 30°C, indicating that reasonable high molecular weights were obtained. Good optical quality films with thickness over 30 μm can be casted from their TCE solutions.

The ^{1}H NMR spectra of polymers **1** and **2** in tetrachloroethane-d$_4$ were very similar to each other. The major peaks are corresponding to the protons of the chromophore and the divinyl benzene moieties. However, the chemical shifts due to the protons of the bipyridyl ligand at 8.0 and 8.5 ppm are still noticeable for polymer **2**, indicating the incorporation of the ruthenium complex into the polymer.
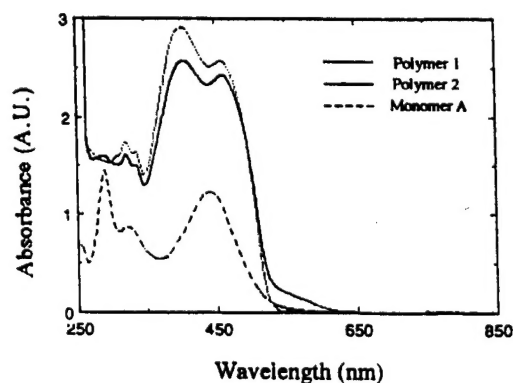

Figure 1.   UV/Vis spectra of monomer **A** and polymers **1, 2**.

The UV-Vis spectra of the polymers are shown in Figure 1. Both polymers **1** and **2** exhibit two major peaks: one at 390 nm which is due to the absorption of the NLO chromophore, the other at 460 nm which is attributed to the absorption of the conjugated backbone. For polymer **2**, however, there is an absorption tail extending beyond 600 nm, which can be assigned to the

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metal-to-ligand charge transfer absorption of the ruthenium complexes. This is a further evidence for the incorporation of the ruthenium complex into the polymer. It also indicates that the incorporation of the ruthenium complex extends the photosensitivity of the polymer to the region of longer wavelengths. By using diode laser (i.e. 690 nm), we can photoexcite the polymer mainly through the MLCT process while the absorptions due to the NLO chromophore and the conjugate backbone can be minimized. It can be noted that a small peak at 290 nm, due to the ligand-centered transition of the two bipyridyl ligand in the ruthenium complexes, exists for polymers **2** while polymer **1** does not have this absorption.

DSC studies showed that polymers **1** and **2** had a similar glass transition temperature at ca. 130 °C. The main chain melting temperature for polymers **1** and **2** was observed at 215 °C, which overlapped with the crosslinking temperature of the conjugated polymer backbone.[13] TGA analysis showed that polymer **1** was stable up to 350 °C while polymers **2** has a small weight loss starting at 270 °C, caused by the loss of the bypyridyl ligands in the ruthenium complexes.

Physical Characterization: The second-order nonlinearity of the poled polymers was demonstrated by the second harmonic generation (SHG) measurement. After corona poling, a SHG coefficient, d_{33}, of 70 pm/V for polymer **2** was obtained at 1064 nm. The poled polymer films also exhibited reasonable thermal and temporal stabilities in their optical nonlinearity. It was found that the SHG signal of polymer **2** was stable up to 80 °C. When the poled polymer film was kept at 60 °C, the SHG signal, after an initial drop, stabilized at an value of 80%. This stability of the nonlinearity allowed us to perform the photorefractive experiments without applying an external electric field.

To further demonstrate the electro-optic effect, the EO coefficient of polymer **2** was measured using a reflection method.[14] An E-O coefficient of 7 pm/V was obtained at 690 nm, a quite high value as compared to other photorefractive polymers. This large nonlinearity arises from the large NLO chromophore composition in the polymers (~70 wt %).

The photoconductivity of the polymers, another necessary condition for PR effect, was measured at a wavelength of 690 nm. As expected, polymer 2 exhibited large photoconductivity. A photoconductivity of 3 x 10^{-10} Ω^{-1} $cm^{-1}/(W/cm^2)$ and a photocharge generation efficiency of 0.2% were obtained under an external electric field of 950 kv/cm. This value is a significant improvement from our previous polymers.[15]

To study the PR effect, a most effective technique is the two beam coupling experiment which is regarded as the standard experiment to confirm the PR response. We performed the two beam coupling experiment at 690 nm (diode laser, s-polarized). The normal of the sample was rotated 35° with respect to the bisector of the writing beams to obtain a non zero projection of the EO coefficient. The transmitted beam intensities were measured with lock-in amplifiers (time constant of the lock-in amplifiers was set at 10 ms) and the data was collected by a computer. At the time of 20 seconds, the two laser beams were overlapped at a pristine spot inside the polymer film. Notice that the intensity of one beam, as a function of time, kept on increasing while that of the other decreasing. The gain and loss was calculated (the ratio of the two incident beam intensities is 1.12) by the following equation: $\Gamma = \frac{1}{L}\ln(\frac{1+\alpha}{1-\beta a})$; where α is the ratio of the intensity modulation $\Delta Is/Is$); β is the intensity ratio of the two incident laser beams (Is/Iq). It was found that polymer **2** exhibited an optical gain higher than 300 cm^{-1}. At the time of 700 seconds, the pump beam was blocked and the transmitted intensity of the other beam went back to the initial value. When the sample was rotated 180 °C along its axis, the gain and the loss beams were switched due to the reversion of the dipole orientation. This result clearly showed that the grating was indeed of photorefractive nature, although the process is rather slow.

By utilizing a known technique,[16] the phase of index grating can be studied. This experiment can furnish further evidences for the photorefractive effect. After forming the grating by intersecting the two laser beams inside the polymer film for a few minutes, the sample plate was translated along the direction parallel to the grating wave vector. The transmitted intensities of the two beams exhibit an oscilating pattern which reflect the spacing and phase of grating. It was

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shown that a 90° phase shift of the index grating over the intensity distribution exists for polymer **2.** This result verified the photorefractive nature of the grating. Since polymer **2** exhibits an absorption coefficient of 102 cm^{-1}, a large net optical gain was obtained in this polymer at a zero external electric field.

Synthesis of Near IR Sensitive PR polymers: The synthetic approach described above is versatile and can be applied to synthesize other metal-containing polymers, such as polymers containing Os-complexes. The advantage to utilize Os-complex as the photosensitizer is that Os-complex has a spin allowed ^{1}MLCT transition at 450 nm and an extremely broad (over 200 nm bandwidth) spin forbidden ^{3}MLCT transitions at around 640 nm (see Figure 2, the UV/vis spectrum for Monomer **B**). The broad absorption which extends beyond 750 nm is very useful for the design of IR sensitive materials. If we polymerize the Os-complex into the conjugated PR polymer system, the resulted polymer could show photorefractivity at wavelengths in the near-IR regions (for example at 780 nm).

The Os-complex (Monomer **B**) was synthesized by reacting the ligand (Compound **7** in Scheme 1) with Os(II)(bpy)$_2$Cl$_2$, which was prepared according to a literature procedure.[17] The resulted Os-complex is black shining powder, which is soluble in common organic solvents such as chloroform, THF, methylene chloride etc.

For a comparison, a polymer with the same molar composition (5 mol % Os-complex) as polymer **2** was synthesized (Polymer **3**) by using the Heck reaction at similar conditions. Polymer **3** is a dark powder which is soluble in NMP, DMF etc. The incorporation of the Os-complex into the polymer backbone can be clearly seen from its UV/vis spectrum. As shown in UV/vis spectrum, there is an absorption tail extending to 600 nm, which can be assigned to the spin allowed transition of the Os-complex Figure 3. The inset of Figure 2 was the UV/Vis spectra of concentrated polymer solutions. It can be clearly seen that polymer **3** has an absorption tail extending to near 800 nm.
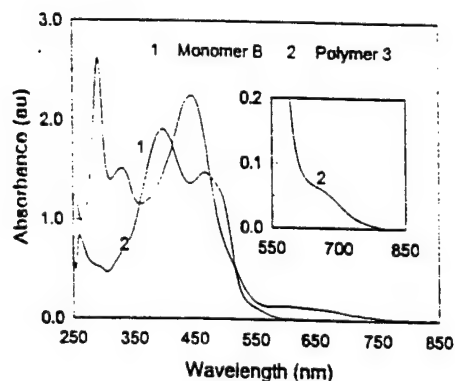
Figure 2. UV/Vis spectra of the Os-complex (in THF solution).

The polymer has a glass transition temperature of 110 °C and a crosslinking temperature of 175 °C. TGA analysis showed two weight losses, one started at 240 °C and the other at 310 °C. The first weight loss (6%) is due to the decomposition of the Os-complex while the second one is due to the decomposition of the backbone.

Two beam coupling experiment was performed at 780 nm (30 mW, s-polarized). A polymer film with a thickness of 5.09 μm was prepared. The sample was tilted 30° and the angle between the two incident laser beams was 46.4°, which gave a grating spacing (Λ) of 0.24 μm (the polymer has a refractive index of 1.7486 at 780 nm). The data was taken under a zero external field after overlapping the two laser beams inside the sample for four to five minutes. The asymmetric energy exchange was clearly observed. The corresponding optical gain was calculated to be 80.4 cm^{-1}. Although net optical gain was not realized (α was measured to be 186 cm^{-1}), the observation of such a photorefractive reponse at near IR region is still very interesting. Net optical gain may be obtainable for polymers with less Os-complex concentrations.
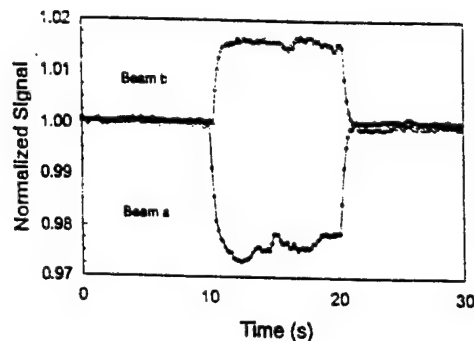
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Figure 3. Asymmetric energy exchange in the 2BC experiment for polymer **5** at zero external field.

PR Polymers Based on Alkyl-Substituted PPV: As mentioned earlier, the alkoxy-substituted PPV has a π-π* transition at a maximum of 450 nm, which is still partially overlapped with the MLCT transition of the Ru-complexes. It is understandable that any absorption at the working laser wavelength (690 nm in our case for Ru-complex containing polymers) by the component other than the photocharge generator is a waste of photons and should be minimized. It is known that the π-π* transition of alkyl-substituted PPVs occurs at shorter wavelengths. If we can change the alkoxy substitutes in polymer 2 to alkyls, we should be able to decrease the absorption of the PPV backbones significantly. For this purpose, a new chromophore (monomer **D**) was synthesized as shown in Scheme 4. The polymer structures were shown in Scheme 5. Two polymers were synthesized: polymer **4** without Ru-complex and polymer **5** with 5 mol % Ru-complex.

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Scheme 4. Synthesis of monomer **D.**
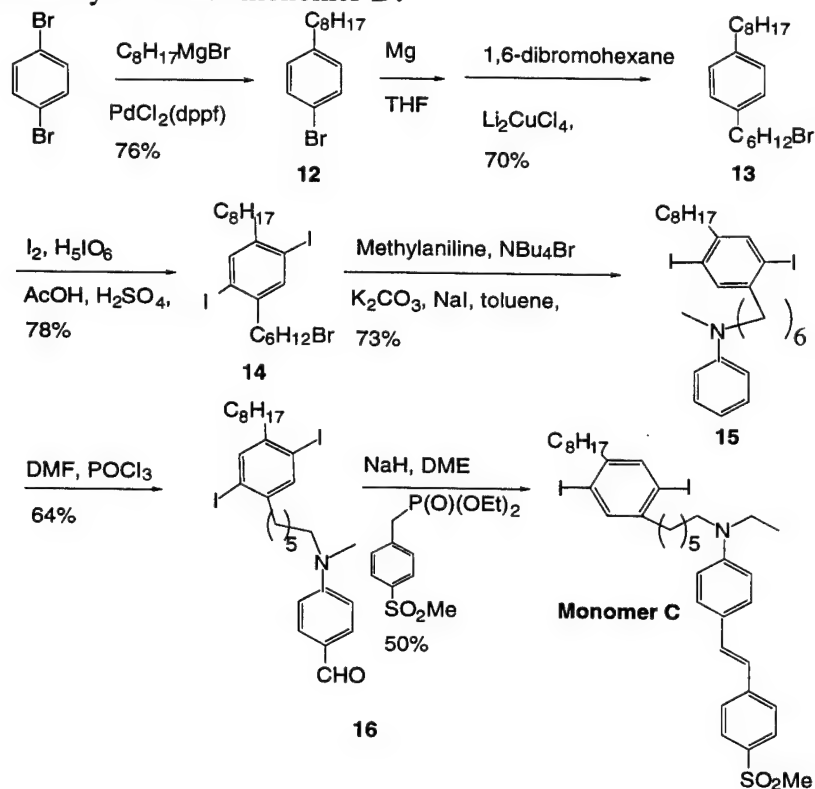
Scheme 5. Synthesis of polymers with alkyl side chains.

Polymer **3.** x = 1, y = 0

Polymer **4.** x = 0.95, y = 0.05

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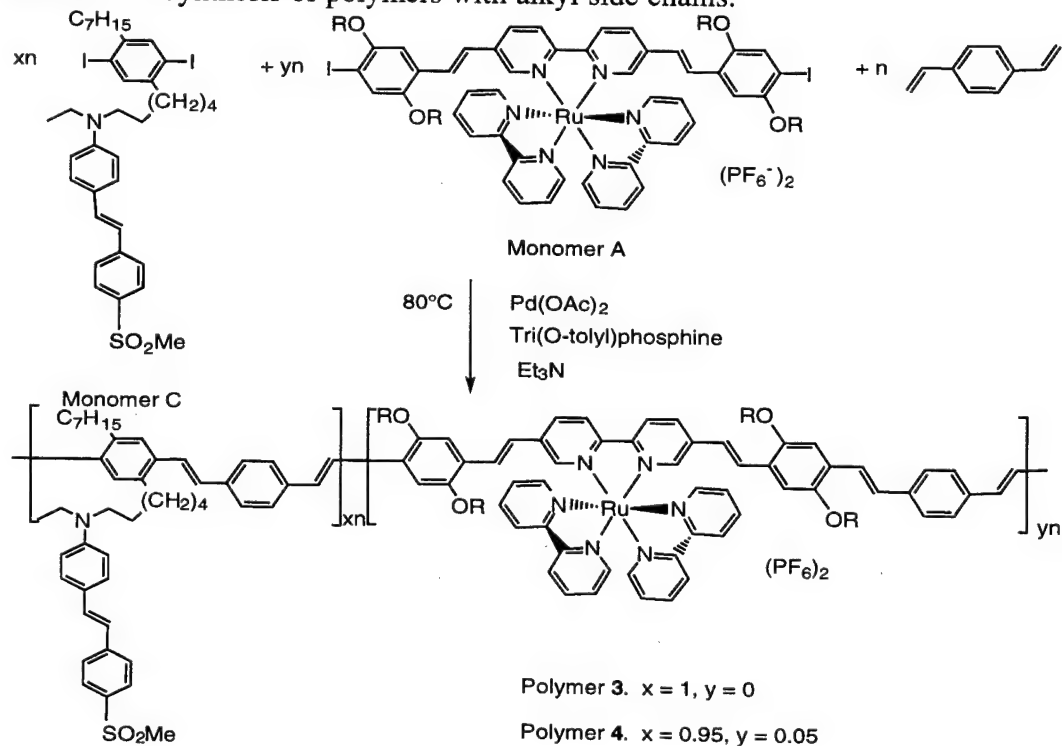
Unlike polymers **1** and **2**, polymers **4** and **5** are soluble in chloroform and THF. Their molecular weights were measured to be 21 kdalton (Mn, PD = 2.8) and 18 kdalton (Mn, PD = 2.25), respectively, by GPC (polystyrene as standard). The incorporation of the Ru-complex into the polymer backbone was again proved by the ^{1}H NMR spectra, typical chemical shifts at 8.0 and 8.5 ppm due to the bipyridyl ligand protons and at 4.0 ppm due to the -OCH$_2$- protons was observed for polymer **5**.

The UV/Vis spectra of the polymers showed that the absorption due to the PPV backbone overlapped with that of the chromophores, both with a maximum at around 380 nm. Again, polymer **5**, unlike polymer **4**, has an absorption tail extending beyond 600 nm. Since both the chromophores and the PPV backbones essentially have no absorption beyond 500 nm, much smaller absorption coefficient (21.5 cm^{-1}) was obtained for polymer **5**.

Polymers **4** and **5** have a relatively low glass transition temperature of 75 °C. Consequently their SHG stability are not as good as polymers **1** and **2**. However, we were able to prepare thick films sandwiched between two ITO coated glasses. As shown in Figure 3, when an electric field (1000 v over 75 μm thick film) was applied at 20 seconds, the transmitted intensity of one beam increased while that of the other beam decreased with a response time of 10 seconds. Energy exchange of more than 5% between the two beams was observed , which gave an optical gain of 16 cm^{-1}. When the field was turned off at 60 seconds, the intensities of the two beams went back to their original values gradually in 20 seconds. This results demonstrated its photorefractivity. Considering the small field applied (less than 15 V/μm), one would expect higher optical gain values if higher electric fields could be applied.

Study of the structural defects in the Heck reaction and their effects on the photorefractivity: It was found that the ^{1}H NMR spectra of all of our polymers synthesized by the Heck reaction exhibited small peaks which cannot be removed by any purification process. For example, multiple peaks between 0.90~1.35, 6.52 and a peak at 3.73 ppm exist. It is known that

the Heck reaction involved many side reactions which clearly will introduce defects into the conjugated backbone.[18] These defects may play the role of deep trapping centers and thus exert profound effect on the PR performance of the polymers. To identify the structural defects in the conjugate polymers synthesized by the Heck reaction, we carried out model reactions involving similar monomers and styrene as shown in Scheme 6.

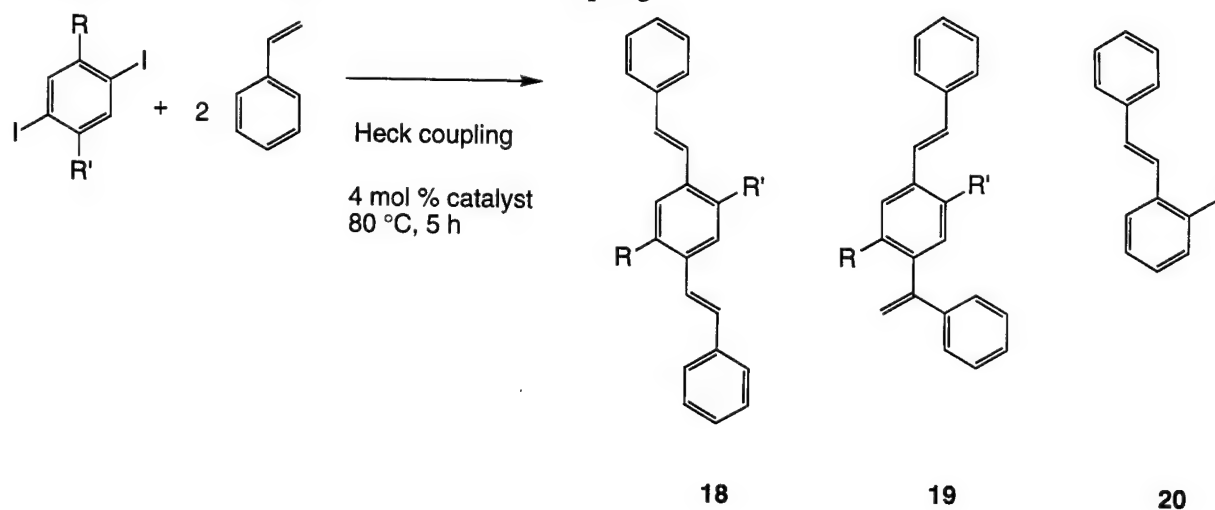**Scheme 6**. Model reactions via the Heck coupling.

**Table I.** Yields of the products in the model reaction.

Entries	R	R'	18	19	20
a	OC_6H_{13}	OC_6H_{13}	85	14	1
b	C_6H_{13}	C_6H_{13}	92	8	---
c	OC_7H_{15}	(structure: N-substituted with SO_2Me stilbene group)	90	10	---

Three diiodo compounds were used to run the model reactions. After completion of the reaction, the mixtures were poured into aqueous solution (5% HCl) and extracted with ethyl ether.

The ^{1}H NMR spectra of the mixture were collected. Based on that, the relative yields of the products were calculated. The results were shown in Table I.

Within 5 hours, the coupling reactions completed for all of three model reactions (no proton peaks corresponding to the diiodo-starting material were observed in the ^{1}H NMR of the reaction mixture). It was found that a significant amount of α-substituted product **19** were obtained in all three cases. The small peaks mentioned above in the ^{1}H NMR spectra of polymers correspond well to the α-substituted structural moieties. These α-substituted units break the conjugation and therefore form stuctural defects. However, the integrations of the peaks of these defects in the ^{1}H NMR spectra of polymers are much smaller than that observed in the model reactions although the exact reason is not very clear.

Scheme 7. Synthesis of monomer **E**.
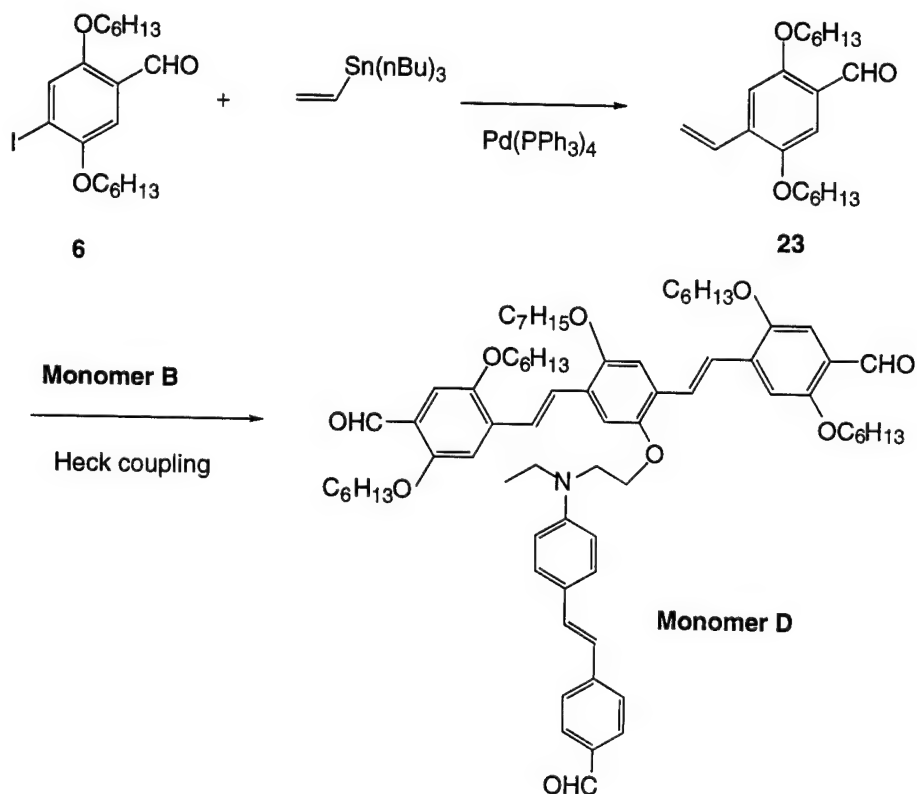
To study the effect of these defects on the polymer properties, we synthesized two conjugated polymers with the same chemical structure by different approaches. As shown in scheme 8, while polymer **7** was synthesized through the Horner-Wittig-Emmons (HWE) reaction.

It is known that tetraethyl xylylenebisphosphonate (compound **22**) reacts with benzaldehyde resulting in only trans products.[10] In addition, the phosphorus product is a phosphate ester and hence soluble in water, which makes it easy to separate it from the olefin product. We found that HWE reaction gave all-trans linear conjugated polymers.

Scheme 8. Synthesis of polymers **8** and **9** via HWE reaction.
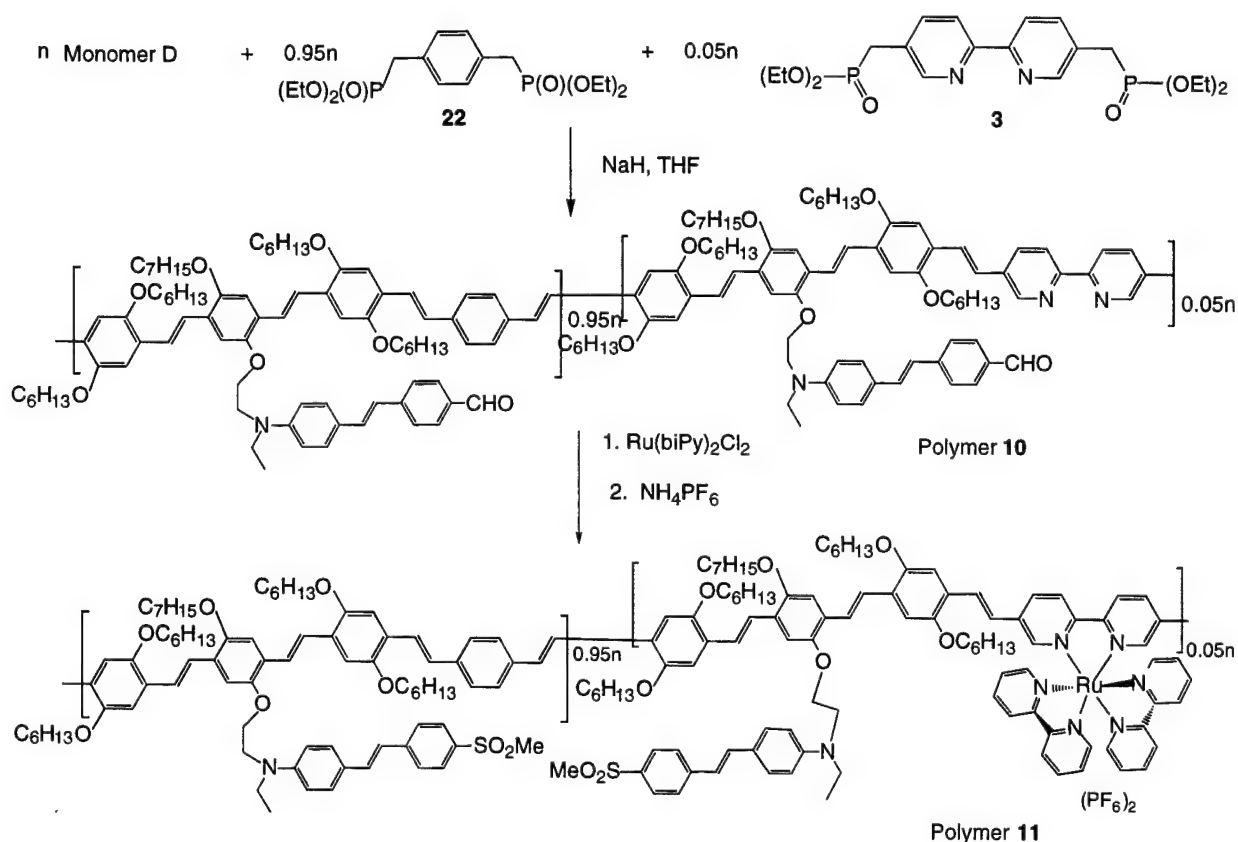
Polymer **6** (Mw = 34 kdalton, intrinsic viscosity = 0.48 dL/g) has a brown color and is soluble in THF, DMF, NMP etc. while polymer **7** (intrinsic viscosity = 0.56 dL/g) was red-colored and insoluble in THF, partially soluble in DMF, NMP etc.

The ^{1}H NMR spectra of the polymers clearly showed that polymer **7** has less structural defects than polymer **6**. The side peaks corresponding to the α coupling structures were observed at 1.02, 1.10, 1.18, 3.74, 5.3, 5.6 ppm for polymer **6** but not for polymer **7**. The UV/Vis spectrum of polymer **7** shows an absorption maximum at 465 nm, a 10 nm red shift compared to that of polymer **6**, which could imply a better conjugation in polymer **7**.

More significant difference came from the thermal properties of these two polymers. As shown in the DSC studies. polymer **7** has a clear backbone melting transition at 270°C and is stable upto 350°C, while polymer **6** shows a broad melting transition at 200°C and starts to decompose at 300°C. These results clearly demonstrate that the bulky properties of the polymers depend strongly on the synthetic approaches. Polymer **7** synthesized by the HWE reaction has more regular linear trans structure and therefore higher crystallinity, and longer absorption maximum.

As a further step, we synthesized the ruthenium complex containing PR polymers via the HWE reaction. As shown in Scheme 8, we utilized the Heck reaction to synthesize monomer **E** from monomer **C**. Considering the uncertainty of the Ru-complex under the harsh reaction condition of the HWE reaction (strong base was used), we chose to synthesize the conjugate polymer first and then coordinate with the ruthenium complex. This approach, of course, lacks the certainty about the yield of the coordination of the ruthenium complexes.

Polymer **8** was synthesized as a red powder. THF was found to be the best solvent for the polymerization and the polymer precipitated out of the reaction mixture in several hours. The final coordination step was carried out in THF. The resulted polymer **9** showed much better solubility in THF, chloroform etc. than polymer **8**.

The ^{1}H NMR spectra of the two polymers (**8** and **9**) showed no clear difference. But UV/Vis spectra do provide some structural information. Polymer **9** showed a backbone absorption maximum at 474 nm, slightly blue-shifted compared to polymer **8** (477 nm), and an absorption tail extending near 600 nm. These results imply that some coordination of the ruthenium complex

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indeed occurred. Another evidence of the coordination comes from the elemental analysis, 0.09% of ruthenium was found in the polymer, which accounts for 12% of the dipyridyl site. This low coordination ratio could be due to the poor solubility of polymer **8**.

Preliminary two beam coupling studies showed encouraging results. A response time of 150 seconds and an optical gain of 99 cm^{-1} were obtained. Indeed, the photorefractive response time is faster than our previous PR polymers made by the Heck reaction (over 500 seconds), although the comparison should be cautious. The smaller optical gain could be due to the incomplete coordination of the ruthenium complexes

Conclusions

We have demonstrated that the hybridized polymers which combined the ionic transition metal complexes and a conjugated polymer backbone bearing NLO chromophores exhibited large photorefractivity. In this system, the conjugated polymer backbone was designed to play the dual role of both transporting channel for the charge carriers and the macroligand to chelate with the transition metal-complex. Ru(II)-tri(bispyridyl) complexe was selected as the photocharge generator because of its metal-to-ligand charge transfer properties. The Heck coupling reaction was successfully applied to synthesize these multifunctional polymers. A large net optical gain (>200 cm^{-1}) at a zero electric field was observed. The synthetic approach is versatile and was extended to the synthesis of PR polymers containing Os-complexes. The resulted polymer showed photorefractivity at a wavelength in the near IR region, which is the first example of IR sensitive PR polymers. This approach also offers opportunity to fine-tune the electronic properties of polymers through easy modification of the polymer structures. Model reactions were studied to elucidate the structural defects caused by the side reactions in the Heck reaction. The effects of these defects on the PR performance of these polymers were evaluated. It was demonstrated that elimination of these defects could enhance the photorefractive response time. This work also indicated a dilemma in choosing polymerization approaches: the Heck reaction introduces

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undesired structural defects in the conjugate backbone. However, it can unambiguously assure the coordination of the transition metal complex, while HWE reaction does in the opposite way. Therefore, a new polymerization method which can not only tolerate transition metal complex, but also give defect-free linear conjugate polymer chain is needed.

Experimental Section

THF and Ethyl ether were purified by distillation over sodium chips and benzophenone. Styrene was distilled over calcium hydride. The p-divinyl benzene was separated from a mixture of p-divinylbenzene and m-divinylbenzene according to the literature procedure.[20] All of the other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise stated.

Syntheses of monomers: The following compounds were synthesized according to literature procedures: 5,5'-dimethyl-2,2' bipyridine **1**,[21] compound **2**,[16] compound **5**.[11]

Compound 3. The mixture of compound **2** (3.00 g, 8.77 mmol) and P(OEt)$_3$ (4.37 g, 26.3 mmol) was stirred at 125 °C for 4 hours. The excess amount of P(OEt)$_3$ was distilled out and the residual solid was recrystallized from chloroform/hexane to give 3.50 g of compound **3** (87%, m.p. 99-100 °C). ^{1}H NMR (CDCl$_3$, ppm): δ 1.27 (m, 12 H, -CH$_3$), 3.16 (d, J = 21.71 Hz, 4 H, -CH$_2$-P-), 4.03 (m, 8 H, -OCH$_2$-), 7.73 (d, J = 8.16 Hz, 2 H, aromatic protons), 8.27 (d, 8.07 Hz, 2 H, aromatic protons), 8.50 (s, 2 H, aromatic protons). Anal. Calcd for C$_{20}$H$_{30}$N$_2$O$_6$P$_2$: C, 52.63; H, 6.62; N, 6.14. Found: C, 52.44; H, 6.54; N, 6.07.

Compound 6. The BuLi (14.33 ml, 2.5 M solution in hexane, 35.82 mmol) in ether (50 ml) was added dropwise into an ether solution containing 2, 5 - dialkoxy 1, 4-diiodo benzene (R = C$_7$H$_{15}$, 20.00 g, 35.82 mmol, 75 ml ether) at 0 °C. After the completion of the addition of BuLi, DMF (3.93 g, 53.76 mmol) in 15 ml of ether was added dropwise into the solution. The resulting mixture was stirred at room temperature for 2 hours, and was then poured into water (200 ml). The ether layer was washed three times with water and dried over MgSO$_4$. The ether was then

removed by vacuum evaporation. The resulting liquid was dissolved in hexane and stored in a refrigerator. Compound **6** crystallized out of the solution (10.70 g, 65% yield, mp 51.5-52°C). ^{1}H NMR (CDCl$_3$, ppm): δ 0.89 (t, J = 6.56 Hz, 6 H, -CH$_3$); 1.31 (m, 8H, **-CH$_2$CH$_2$**-CH$_3$); 1.36 (m, 4H, -CH$_2$CH$_2$CH$_2$CH$_3$); 1.46 (m, 4 H, -CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$); 1.80 (quartet, J = 6.89 Hz, 4H, -OCH$_2$CH$_2$-); 3.97 (t, J = 5.47 Hz, 2 H, -OCH$_2$-); 3.99 (t, J = 5.65 Hz, 2 H, -OCH$_2$-); 7.14 (s, 1 H, aromatic proton, ortho to CHO); 7.4 (s, 1 H, aromatic proton, meta to CHO); 10.34 (s, 1H, -CHO). ^{13}C NMR (CDCl$_3$, ppm): 14.2, 22.8, 26.1, 29.2, 29.3, 31.9, 69.6, 70.0, 108.9, 124.6, 125.3, 152.3, 155.9, 189.2. Anal. Calcd for C$_{21}$H$_{33}$O$_3$I: C, 54.79; H, 7.22; I, 27.56. Found: C, 54.86; H, 7.21; I, 27.49.

Compound 7. Sodium hydride (0.24 g, 9.81 mmol) was added to a solution of compound **6** (3.01 g, 6.65 mmol) in DME (20 ml). The resulting suspension was stirred for 5 minutes. Compound **3** (1.49 g, 3.27 mmol) in DME (10 ml) was then added dropwise at room temperature. The mixture was refluxed overnight. After the solution cooled down to room temperature, water was added. The resulting mixture was stirred for 5 minutes and the crude product was separated by filtration. Recrystalization from dichloromethane/methanol gave 2.20 g of pure compound **7**. (83%, m.p. 84-85 °C). ^{1}H NMR (CDCl$_3$, ppm): d 0.9 (m, 12 H, -CH$_3$); 1.3-1.9 (m, 40H, aliphatic protons); 3.95 (t, J = 6.2 Hz, 4 H, -OCH$_2$-); 4.01 (t, J = 6.2 Hz, 4 H, -OCH$_2$-); 6.99 (s, 2 H, aromatic protons meta to Iodo); 7.10 (d, J = 16.47, 2 H, vinyl protons); 7.26 (s, 2 H, aromatic protons ortho to Iodo); 7.44 (d, J = 15.56 Hz, 2 H, vinyl protons); 7.92 (**dd, J = 8.42 (1.73) Hz**, 2 H, 4-pyridine protons); 8.34 (d, J = 8.24 Hz, 2 H, 3-pyridine protons); 8.71 (s, 2 H, 2-pyridine protons). ^{13}C NMR (CDCl$_3$, ppm): 14.4, 22.8, 26.3, 29.3, 29.5, 32.0, 69.6, 70.3, 86.9, 110.0, 120.9, 123.7, 125.5, 126.8, 133.4, 148.3, 151.6, 152.3, 154.6. Anal. Calcd for C$_{54}$H$_{74}$N$_2$O$_4$I$_2$: C, 60.67; H, 6.98; N, 2.62. Found: C, 60.90; H, 6.93; N, 2.59.

Monomer A. A solution of 0.1500 g of compound **7** (0.14 mmol) in 10 ml of methoxyethanol was heated to 100 °C. Cis-dichlorobis(2,2'-bipyridine)ruthenium(II) hydrate (

0.0679 g, 0.14 mmol) in ethanol (10 ml) was added. The ethanol was then evaporated and the resulting solution was stirred at 140 °C for 3 hours. After cooling down to room temperature, the solution was added into a solution of $(NH_4)PF_6$ (0.2283 g) in water (50 ml). An orange solid was collected by filtration and recrystallized from THF/hexane to give 0.1300 g of the desired product. (53%, m.p. 234-235 °C). ^{1}H NMR (CDCl$_3$, ppm): d 0.86 (t, J = 6.56 Hz, 12 H, -CH$_3$); 1.28-1.78 (m, 40 H, aliphatic protons); 3.87-4.01 (m, 8H, -OCH$_2$-); 6.93 (d, J = 16.45 Hz, 2 H, vinyl protons); 7.07 (s, 2 H, aromatic protons meta to iodo); 7.20 (s, 2 H, aromatic protons ortho to iodo); 7.38 (d, J = 16.44 Hz, 2H, vinyl protons); 7.47 (t, J = 6.63 Hz, 2H, aromatic protons on the dipyridine ligand); 7.51 (t, J = 6.22 Hz, 2 H, aromatic protons on the dipyridine ligand); 7.67 (s, 2 H, aromatic protons); 7.81 (d, J = 5.28 Hz, 4 H, aromatic protons); 7.91 (m, 4 H, aromatic protons); 8.07 (d, J = 8.47 Hz, 2 H, aromatic protons); 8.15 (d, J = 8.67 Hz, 2 H, aromatic protons); 8.22 (t, 7.82 Hz, 2 H, aromatic protons);. Anal. Calcd for C$_{74}$H$_{90}$N$_6$O$_4$I$_2$P$_2$F$_{12}$Ru: C, 50.14; H, 5.12; N, 4.74; I, 14.32. Found: C, 50.17; H, 5.15; N, 4.73; I, 14.44.

Compound 9. To a solution of 2,5-dimethoxy 1,4-diiodobenzene (10.00 g, 25.6 mmol) in dichloromethane (50 ml), cooled in dry ice/acetone, was added dropwise the BBr$_3$ (26.50 g, 105.8 mmol) in dichloromethane (15 ml). The resulting solution was stirred at room temperature overnight and then poured into ice water. The white precipitate was collected by filtration and recrystalized from THF/hexane to yield compound **9** (8.1 g, 87%, m.p. 192-194 °C). ^{1}H NMR (CDCl$_3$, ppm): δ 7.10 (s, 2 H, aromatic protons); 9.72 (s, 2 H, -OH).

Compound 10. To the solution of compound **9** (7.00 g, 19.34 mmol) in DMSO (50 ml), potassium hydroxide powder (3.25 g, 58.02 mmol) was added. A solution of bromohexane (3.19 g, 19.34 mmol) in DMSO (10 ml) was then added immediately. The resulting mixture was stirred at room temperature overnight and then poured into water. The white solid (mainly dialkoxy-side product) was filtered out and the filtrate was neutralized by hydrochloric acid. Product was collected by filtration and further recrystalized from hexane (refrigerate) to give

compound **10**.(5.00 g, 56%, m.p. 48-50°C). ^{1}H NMR (CDCl$_3$, ppm): δ 0.91 (m, 3 H, -CH$_3$); 1.34-1.80 (m, 8 H, aliphatic protons); 3.88 (t, J = 6.16 Hz, 2 H, -OCH$_2$-); 4.88 (b, 1 H, -OH); 6.97 (s, 1 H, aromatic protons ortho to OH); 7.35 (s, 1 H, aromatic protons meta to OH).

Monomer C. Diethy azodicarboxylate(DEAD) (1.0 0g, 5.7 mmol) in THF (5 ml) was added into a solution of compound **10** (1.70 g, 3.8 mmol), 4-(2-hydroxy ethyl) ethyl amino-4'-sulphone stilbene (compound **11**, 1.30 g, 3.8 mmol) and triphenyl phosphine (1.50 g, 5.7 mmol) in THF (20 ml). The resulting mixture was stirred overnight and then concentrated to less than 5 ml. The solution was poured into hot methanol and filtered while it was still hot. The resulting yellow solid was purified by chromatography (CH$_2$Cl$_2$ as eluent) and then recrystallized from acetone/methanol. The resulted product was light yellow-colored crystal.(2.05 g, 70%, m.p.145-147 °C). ^{1}H NMR (CDCl$_3$, ppm): δ 0.90 (m, 3H, -CH$_3$ in alkoxy); 1.23 (t, J = 7.01 Hz, 3 H, -CH$_3$ on chromophore), 1.33-1.79 (m, 8H, aliphatic protons), 3.03 (s, 3H, -SO$_2$CH$_3$), 3.56 (m, 2H, N-CH$_2$-CH$_3$), 3.78 (m, 2H, -CH$_2$-CH$_2$-N), 3.90 (m, 2H, -OCH$_2$- on alkoxy side chain), 4.07 (t, J = 5.46 Hz, 2H, -OCH$_2$-CH$_2$N-), 6.69 (d, J = 8.34 Hz, 2H, aromatic protons), 6.86 (d, J = 16.33 Hz, 1H, vinyl proton), 7.12 (s, 1H, aromatic protons), 7.13 (d, J = 16.56 Hz, 1H, vinyl proton), 7.37 (d, J = 8.59 Hz, 2H, aromatic protons), 7.55 (d, J = 8.26 Hz, 2H, aromatic protons), 8.01 (d, J = 7.91 Hz, 2H, aromatic protons). ^{13}C NMR (CDCl$_3$, ppm): 12.6, 14.4, 22.8, 26.2, 29.2, 29.3, 32.0, 44.9, 46.0, 49.6, 68.1, 70.5, 86.2, 86.5, 112.0, 121.8, 122.7, 122.9, 124.3, 126.5, 127.9, 128.8, 132.9, 137.7, 144.0, 148.0, 152.6, 153.5. Anal. Calcd for C$_{31}$H$_{37}$NO$_4$SI$_2$: C, 48.13; H, 4.82; N, 1.81. Found: C, 48.22; H, 4.78; N, 1.77.

Monomer B. To the solution of compound **7** (0.20 g, 0.187 mmol) in ethylene glycol (15 ml), heated to 120°C was added cis-dichlorobis(2,2'-bipyridine)osmium(II) (0.10 g, 0.187 mmol) in 5~10 ml ethylene glycol. The resulted solution was stirred at 140 °C for 48 hours. After cooling down to room temperature, the solution was concentrated to 10 ml and then added into a solution of (NH$_4$)PF$_6$ (0.25 g) in 80 ml water. A dark solid was collected by filtration and recrystallized from CH$_2$Cl$_2$/MeOH to give 0.2 g of product as black shining crystal (57%). ^{1}H

NMR (CDCl$_3$, ppm): d 0.85 (t, J = 6.56 Hz, 12 H, -CH$_3$); 1.20-1.55 (m, 32 H, aliphatic protons); 1.73 (m, 8H, -CH$_2$-); 3.86 (t, J = 5.33 hz, 4H, -OCH$_2$-); 3.97 (t, J = 5.6 Hz, 4H, -OCH$_2$-); 6.90 (d, J = 16.40 Hz, 2 H, vinyl protons); 7.04 (s, 2H, aromatic protons meta to iodo); 7.19 (s, 2H, aromatic protons ortho to iodo); 7.31-7.34 (m, 4H, 2 vinyl protons and 2 ArH); 7.37 (t, J = 6.82 Hz, 2H, ArH); 7.56 (s, 2H, ArH); 7.66-7.70 (m, 8H, ArH); 7.90 (d, J = 8.29 Hz, 2H, ArH); 8.15 (d, J = 8.34 Hz, 2H, ArH); 8.21 (t, J = 5.70 Hz, 4H, ArH);. Anal. Calcd for C$_{74}$H$_{90}$N$_6$O$_4$I$_2$P$_2$F$_{12}$Os: C, 47.74; H, 4.87; N, 4.51. Found: C, 47.67; H, 4.88; N, 4.53.

Compound 12. To a vacuum-dried two neck flask was added 1.89 g of Mg (0.0777 mol) and 30 ml of ether. Octylbromide (15.00 g, 0.0777mol) in 20 ml of ether was then added into the above suspension in such a rate that the reaction mixture maintained self-refluxing. After the addition was completed, the mixture was further refluxed in an oil bath for half an hour. The solution was then transfered into an addition funnel and added dropwise into a mixture containing 1,4-dibromobenzene (19.73 g, 0.0777 mol), PdCl$_2$(dppf) (0.60 g, 0.7 mmol) and 40 ml of ether. The resulted mixture was refluxed overnight and then poured into water. After removal of the catalyst residue (red precipitate) by filtration, the filtrate was extracted with ethyl ether. The organic layer was washed with water, dried (MgSO$_4$) and the solvent was evaporated. The resulted liquid was distilled to give 17 g of product as colorless liquid (76%, b.p: 91-92°C/0.8mmHg). ^{1}H NMR (CDCl$_3$, ppm): δ 0.87 (t, J = 6.79 Hz, 3H, -CH$_3$), 1.28 (m, 10 H, alkyl protons), 1.56 (m, 2 H, alkyl protons), 2.53 (t, J = 7.31 Hz, 2 H, benzyl protons), 6.89 (d, J = 7.63 Hz, 2H, aromatic protons), 7.32 (d, J = 7.72 Hz, 2 H, aromatic protons).

Compound 13. To a suspension containing Mg (0.90 g, 37.14 mmol), one tiny crystal of iodine and THF (10 ml) was added 1 ml of compound **12** (10.00 g, 37.14 mmol). After stiring for a couple of minutes, the mixture started to reflux. The rest of the compound 12 was then added to the mixture in such a rate as to maintain the refluxing. After the addition was finished, the mixture was refluxed for another half an hour. The resulted greeniard reagent was transferred into an addition funnel and added dropwise into a mixture containing 1,6-dibromohexane (9.06 g,

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37.14 mmol), Li$_2$CuCl$_4$ (3.71 ml of 0.1M THF solution, 37.14 mmol) and 20 ml of THF at 5-10°C. The resulted mixture was stirred overnight at room temperature and then poured into water. The mixture was extracted with methylene chloride. The organic layer was washed with water, aquaous NaHCO$_3$ solution and water again. It was then dried with MgSO$_4$. After removal of the solvent, the resulted liquid was purified by running through a short filtration column (hexane as the eluent), 9.02 g of pure product was obtained as colorless liquid.(70%) ^{1}H NMR (CDCl$_3$, ppm): δ 0.87 (t, J = 6.79 Hz, 3 H, -CH$_3$), 1.24-1.34 (m, 12 H, alkyl protons), 1.44 (m, 2 H, alkyl protons), 1.59 (m, 4 H, alkyl protons), 1.83 (m, 2 H, alkyl protons), 2.55 (t, J = 7.20 Hz, 4 H, benzyl protons), 3.36 (t, J = 6.34 Hz, 2 H, -CH$_2$Br), 7.02 (s, 4 H, aromatic protons).

Compound 14. A mixture containing compound **13** (9.00 g, 25.47 mmol), iodine (5.19 g, 20.47 mmol), H$_5$IO$_6$ (2.332 g, 10.23 mmol), acetic acid(17 ml), 30% sulphuric acid (3 ml) and CCl$_4$ (8 ml) was stirred at 80 °C for 48 h. It was then poured into aquaous solution of NaHSO$_3$ and extracted with methylene chloride. The organic layer was washed with water, dried (MgSO$_4$) and the solvent was evaporated. The resulted liquid was purified by flash chromatogaphy (hexane as the eluent) to give 11.8 g of product (78%). ^{1}H NMR (CDCl$_3$, ppm): δ 0.87 (t, J = 6.79Hz, 3H, -CH$_3$), 1.24-1.34 (m, 12H, alkyl protons), 1.46-1.59 (m, 6H, alkyl protons), 1.83 (m, 2H, alkyl protons), 2.55 (t, J = 7.20Hz, 4H, benzyl protons), 3.36 (t, J = 6.34Hz, 2H, -CH$_2$Br), 7.52 (s, 2H, aromatic protons).

Compound 15. A solution of compound **14** (4.00 g, 6.71 mmol), N-methyl aniline (1.078 g, 10.07 mmol), potassiun carbonate (1.85 g, 13.42 mmol), tetrabutylammonium bromide (0.11 g, 0.34 mmol) and sodium iodide (2.02 mg, 0.013 mmol) in toluene (5 ml) was stirred under refluxing overnight. Diethyl ether (25 ml) and water (25 ml) were then added. The organic layer was separated and dried over magnesium sulfate. After removal of the solvent, the residue liquid was purified by chromatography (methylene chloride as eluent) to give 3.1g of product as colorless liquid (73%). ^{1}H NMR (CDCl$_3$, ppm): δ 0.87 (t, J = 6.79Hz, 3H, -CH$_3$), 1.26-1.37 (m, 14H, alkyl protons), 1.51-1.58 (m, 6H, alkyl protons), 2.56 (t, J = 6.50Hz, 4H, benzyl

protons), 2.90 (s, 3H, -NCH$_3$), 3.28 (t, J = 7.15Hz, 2H, -CH$_2$N), 6.40 (t, J = 7.95 Hz, 3H, aromatic protons), 7.17 (d, J = 7.08Hz, 2H, aromatic protons), 7.52 (s, 2H, aromatic protons).

Compound 16. Phosphorus oxychloride (1.21 g, 7.919 mmol) was added dropwise to DMF (5 ml, 64.6 mmol) at 0 °C. The solution was stirred at 0°C for 1 hour and then at 25°C for another 1 hour. Compound **15** (5.00 g, 7.919 mmol) in 5 ml of DMF was then added dropwise to the mixture. The resulted solution was stirred at 80°C overnight. After being cooled down to room temperature, the solution was poured into cold water and neutralized with NaAc. The mixture was extracted with methylene chloride. The organic layer was washed with water and then dried. After removal of the solvent, hexane was added to the liquid residue. The product crystalized out and collected by filtration as white solid. (3.34 g, 64%, mp: 70-71°C). ^{1}H NMR (CDCl$_3$, ppm): δ 0.88 (t, J = 6.48 Hz, 3H, -CH$_3$), 1.27-1.64 (m, 20H, alkyl protons), 2.55-2.59 (m, 4H, benzyl protons), 3.02 (s, 3H, -NCH$_3$), 3.38 (t, J = 7.36Hz, 2H, -CH$_2$N), 6.63 (d, J = 8.61 Hz, 2H, aromatic protons), 7.52 (s, 2H, aromatic protons), 7.66 (d, J = 8.61Hz,2H, aromatic protons), 9.65 (s, 1H, aldehyde proton).

Monomer D. Sodium hydride (0.40 g, 16.51 mmol) was added to a solution of compound **16** (7.26 g, 11.01 mmol) in 1,2-dimethoxyethane (DME) (10 ml). The suspension was stirred for 5 min. and diethyl 4-(methylsulfonyl)benzyl phosphate (3.37 g, 11.01 mmol) in 5 ml of DME was then added dropwise. The resulted solution was stirred at 80°C overnight and then poured into water. The mixture was extracted with methylene chloride. The organic layer was washed with water and dried. After removal of the solvent, the resulted mixture was purified by chromatography (hexane:ethyl acetate=2:1 as eluent) and recrystalization from ether to give 1.8 g of product as greenish yellow solid (50%, mp: 94-95°C). ^{1}H NMR (CDCl$_3$, ppm): δ 0.87 (t, J = 6.48Hz, 3H, -CH$_3$), 1.23-1.60 (m, 20H, alkyl protons), 2.57-2.58 (m, 4H, benzyl protons), 2.96 (s, 3H,--SO$_2$CH$_3$), 3.03 (s, 3H, -NCH$_3$), 3.33 (t, J = 6.60Hz, 2H, -CH$_2$N), 6.62 (d, J = 8.15 Hz, 2 H, aromatic protons), 6.84 (d, J = 16.13 Hz, 1H, vinyl proton), 7.11 (d, J = 16.20 Hz, 1 H, vinyl proton), 7.36 (d, J = 8.39 Hz, 2 H aromatic protons), 7.53-7.55 (m, 4 H, aromatic

protons), 7.80 (d, J = 7.97 Hz, 2 H, aromatic protons). Anal. Calcd for $C_{36}H_{47}SNI_2O_2$: C, 53.27; H, 5.84; N, 1.73. Found: C, 53.21; H, 5.86; N, 1.67.

Polymerization via the Heck coupling reaction. A typical polymerization was exemplified by the synthesis of polymer **2**: Triethylamine (0.19ml, 1.36mmol) was added to a solution of monomer **A** (0.0458 g, 0.0258 mmol), Monomer **B** (0.4000 g, 0.517 mmol), p-divinylbenzene (0.0707 g, 0.543 mmol), Pd(OAc)₂ (4.9 mg,0.0217 mmol), and tri-0-tolylphospine (32.9 mg, 0.108 mmol) in 5-10 ml DMF. The resulting mixture was stirred at 80 ℃ overnight under a nitrogen atmosphere and was then poured into methanol. The precipitated polymer was collected by filtration, redissolved in tetrchloroethane and reprecipitated into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol for 24 h and dried under a vacuum at 50 °C for 2 days.

Polymer 1. ^{1}H NMR (CDCl₂-CDCl₂, ppm): δ 0.88 (broad, 3H, -CH₃ in alkoxyl chain), 1.21 (b, 3H, -CH₃ in chromophore), 1.38, 1.49, 1.71, 1.80 (4 broad peaks, each has 2H, methylene protons), 2.87 (m, 3H, -SO₂Me), 3.48 (b, 2H, -NCH₂CH₃) 3.79 (b, 2H, -NCH₂CH₂O-), 4.00 (b, 2H, -OCH₂- in alkoxyl chain), 4.20 (b, 2H, -OCH₂CH₂N-), 6.75 (b, 4H, aromatic protons), 7.02 (b, 5H, vinyl protons), 7.38 (b, 5H, 4 aromatic and 1 vinyl protons), 7.46 (b, 4H, aromatic protons), 7.69 (m, 2H, aromatic protons). Anal. Calcd. for $C_{41}H_{45}NO_4S$: C, 76.04; H, 6.96; S 4.94. Found: C, 74.38; H, 7.00; S, 5.09

Polymer 2. ^{1}H NMR spectra of polymer 2 is very similar to that of polymer 1 except some small peaks due to the ruthenium complex (8.00, 8.5ppm). Anal. Calcd. for $C_{43.15}H_{47.65}N_{1.25}O_4S_{0.95}P_{0.1}F_{0.6}Ru_{0.05}$: C, 74.28; H, 6.83; N, 2.49; Ru, 0.69. Found: C, 73.36; H, 6.98; N, 2.67; Ru, 0.55.

Polymer 3. ^{1}H NMR spectra of polymer **5** is very similar to that of polymer **3** except some small peaks due to the osmium complex (4.0, 8.00, 8.5 ppm). Anal. Calcd. for $C_{47.9}H_{57.15}N_{1.25}O_{2.1}S_{0.95}P_{0.1}F_{0.6}Os_{0.05}$: C, 74.02; H, 6.98; N, 2.38. Found: C, 71.48; H, 6.73; N, 2.36.

Polymer 4. ^{1}H NMR (CDCl$_3$, ppm): δ 0.87 (broad, 3H, -CH$_3$ in alkyl chain), 1.19-1.16 (b, 20H, aliphatic protons), 2.74 (b, 4H, benzyl protons), 2.92 (b, 3H, -SO$_2$Me), 2.99 (b, 3H, -NCH$_3$), 3.31 (b, 2H, -NCH$_2$-), 6.59 (b, 2H, aromatic protons), 6.99 (m, 1H, vinyl protons), 7.02 (b, 2H, aromatic protons), 7.07 (d, J = 16.85 Hz, 1H, vinyl proton), 7.32 (b, 2H, aromatic protons), 7.40 (b, 4H, vinyl protons), 7.49 (b, 6H, aromatic protons), 7.77 (m, 2H, aromatic protons). Anal. Calcd. for C$_{46}$H$_{55}$SNO$_2$: C, 80.54; H, 8.08; N, 2.04. Found: C, 80.50; H, 8.02; N, 2.08.

Polymer 5. ^{1}H NMR spectra of polymer **5** is very similar to that of polymer **4** except some small peaks due to the ruthenium complex (4.0, 8.00, 8.5 ppm). Anal. Calcd. for C$_{47.9}$H$_{57.15}$N$_{1.25}$O$_{2.1}$S$_{0.95}$P$_{0.1}$F$_{0.6}$Ru$_{0.05}$: C, 78.38; H, 7.85; N, 2.38, Ru, 0.67 Found: C, 76.48; H, 7.72; N, 2.41, Ru, 0.50

Compound 21. Compound **21** was synthesized from compound **5** (see chapter four) by a similar approach as the synthesis of compound **6** (2 eq. of butyl lithium was used). mp. 74-75°C. ^{1}H NMR (CDCl$_3$, ppm): 0.90 (t, J = 6.50 Hz, 6H, -CH$_3$), 1.33 (m, 8H, methylene protons), 1.46 (m, 4H, methylene protons), 1.79-1.84 (m, 4H, methylene protons), 4.05 (t, J = 6.16 Hz, 4h, -OCH$_2$-), 7.37 (s, 2H, aromatic protons), 10.44 (s, 2H, aldehyde protons). Anal. Calcd for C$_{20}$H$_{30}$O$_4$: C, 71.82; H, 9.04; O, 19.14. Found: C, 71.69; H, 9.11.

Compound 22. The mixture of α,α'-dibromo-p-xylene (4.73 g, 17.99 mmol) and P(OEt)$_3$ (8.97 g, 53.98 mmol) was stirred at 120 °C for 4 hours. The excess amount of P(OEt)$_3$ was distilled out. The residual liquid solidified to give the product as a white solid. (6.10 g, 90%, mp. 73-74°C). ^{1}H NMR (CDCl$_3$, ppm): 1.23 (t, J = 6.80 Hz, 12H, -CH$_3$), 3.10 (d, J = 20.51Hz, 4H, benzyl protons), 3.96-3.99 (m, 8H, -OCH$_2$-), 7.19 (s, 4H, aromatic protons). Anal. Calcd for C$_{16}$H$_{28}$O$_6$P$_2$: C, 50.79; H, 7.46; O, 25.37. Found: C, 50.69; H, 7.44.

Compound 23. A mixture of compound **6** (0.60 g, 1.388 mmol), vinyl tributyltin (0.44 g, 1.388 mmol) and Pd(PPh$_3$)$_4$ (0.032 g, 0.0278 mmol) in DMF (8 ml) was stirred at 100 °C for four hours. After cooling down to room temperature, the mixture was filtered and the filtrate was

poured into water. After extraction with ethyl ether, the organic layer was collected and dried over MgSO$_4$. After removal of the solvent, the crude product was purified by chromatography (hexane:ethyl acetate = 20:1 as eluent) to give the product. (0.24 g, 52%, mp. ??) ^{1}H NMR (CDCl$_3$, ppm): 0.86-0.93 (m, 6H, -CH$_3$), 1.26-1.46 (m, 12H, methylene protons), 1.75-1.83 (m, 4H, methylene protons), 3.95 (t, J = 6.51 Hz, 2H -OCH$_2$-), 4.04 (t, J = 6.38 Hz, 2H, -OCH$_2$-), 5.38 (d, J = 11.30Hz, 1H, vinyl proton), 5.80 (d, J = 17.71Hz, 1H, vinyl proton), 7.01 (m, 2H, 1 vinyl and 1 aromatic protons), 7.24 (s, 1H, aromatic proton), 10.36 (s, 1H, -CHO).

Monomer E. The typical Heck reaction condition as for polymerization was applied. Product was purified by chromatography (H:EA=10:1 as eluent) and recrystalized from methylene chloride/methanol. Yield: 38%, mp. 123-124°C. ^{1}H NMR (CDCl$_3$, ppm): δ 0.87-0.91 (m, 15H, -CH$_3$ in alkoxy); 1.23 (t, J = 7.08 Hz, 3 H, -CH$_3$ on chromophore), 1.27-1.38 (m, 22H, aliphatic protons), 1.47-1.55 (m, 10H, aliphatic protons), 1.80-1.87 (m, 10H, aliphatic protons), 3.04 (s, 3H, -SO$_2$CH$_3$), 3.51 (t, J = 7.04Hz, 2H, N-CH$_2$-CH$_3$), 3.81 (t, J = 5.60 Hz, 2H, -CH$_2$-CH$_2$-N), 3.97-4.08 (m, 10H, -OCH$_2$- on alkoxy side chain), 4.22 (t, J = 5.81 Hz, 2H, -OCH$_2$-CH$_2$N-), 6.70 (d, J = 8.57 Hz, 2H, aromatic protons), 6.74 (d, J = 16.39 Hz, 1H, vinyl proton), 7.02 (d, J = 16.23, 1H, vinyl proton), 7.08 (d, J = 6.56Hz, 2H, aromatic protons), 7.10 (d, J = 15.50Hz, 2H, vinyl protons), 7.25 (s, 1H, aromatic proton), 7.28 (s, 2H, aromatic protons), 7.30 (s, 1H, aromatic proton), 7.39 (d, J = 16.45Hz, 1H, vinyl proton), 7.44 (s, 1H, aromatic proton), 7.46 (s, 1H, aromatic proton), 7.49 (d, J = 8.06 Hz, 2H, aromatic protons), 7.52 (d, J = 16.56 Hz, 1H, vinyl proton), 7.80 (d, J = 8.15 Hz, 2H, aromatic protons), 10.33 and 10.34 (s, 2H, -CHO). Anal. Calcd. for C$_{74}$H$_{101}$NO$_{10}$S: C, 74.27; H, 8.51; N, 1.17. Found: C, 74.29; H, 8.47; N, 1.21.

Model reaction. The reaction condition was similar to the above. The reaction mixture was poured into 5% hydrochloric acid solution, extracted with ethyl ether. The organic layer was washed with water, dried over MgSO$_4$ and then the solvent was removed. After collecting the ^{1}H NMR, the residue was separated by chromatography (hexane:ethyl acetate = 6:1 as the eluent) to

give compounds **18,19**, and **20**. The relative yield was calculated based on the ^{1}H NMR spectrum. The characterizations of the products were exemplified by entry a (2,5-dihexoxyl-1,4-diiodo benzene as the reactant) as below:

Compound 18. Purified yield, 78%. ^{1}H NMR (CDCl$_3$, ppm): 0.92 (t, J = 6.58 Hz, 6H, -CH$_3$), 1.37 (m, 8H, methylene protons), 1.53 (m, 4H, methylene protons), 1.85 (m, 4H, methylene protons), 4.02 (t, J = 6.21 Hz, 4H, -OCH$_2$-), 7.07 (s, 2H, aromatic protons), 7.08 (d, J = 15.98, 2H, vinyl protons), 7.30 (t, J = 7.40, 6H, aromatic protons), 7.42 (d, J = 16.51, 2H, vinyl protons), 7.47 (d, J = 7.38, 4H, aromatic protons). ^{13}C NMR (CDCl$_3$, ppm): 14.0, 22.6, 25.9, 29.4, 31.6, 69.4, 110.5, 123.4, 126.4, 126.7, 127.3, 128.6, 137.9, 151.0. Anal. Calcs. for C$_{34}$H$_{42}$O$_2$: C, 84.60; H, 8.77. Found: C, 84.72; H, 8.76.

Compound 19. Purified Yield, 11.7% . ^{1}H NMR (CDCl$_3$, ppm): 0.82 (m, 3H, -CH$_3$), 0.92 (m, 3H, -CH$_3$), 1.02 (m, 2H, methylene protons), 1.10 (m, 2H, methylene protons), 1.18 (m, 2H, methylene protons), 1.33 (m, 6H, methylene protons), 1.52 (m, 2H, methylene protons), 1.81 (m, 2H, methylene protons), 3.73 (t, J = 6.11 Hz, 2H, -OCH$_2$-), 3.96 (t, J = 6.03 Hz, 2H, -OCH$_2$-), 5.30 (s, 1H, vinyl proton), 5.60 (s, 1H, vinyl proton), 6.81 (s, 1H, aromatic proton), 7.04 (s, 1H, aromatic proton), 7.07 (d, J = 16.30, 1H, vinyl proton), 7.18-7.31 (m, 8H, aromatic protons), 7.42-7.48 (m, 3H, 2 aromatic protons + 1 vinyl proton). ^{13}C NMR (CDCl$_3$, ppm): δ, 13.99, 22.41, 22.58, 25.29, 25.88, 29.06, 29.39, 31.48, 31.56, 68.96, 69.35, 110.49, 115.27, 115.97, 123.47, 126.40, 126.56, 126.74, 127.16, 127.26, 127.88, 128.51, 128.66, 131.57, 137.88, 141.47, 147.52, 150.63, 150.72. Mass spectra m$^+$/e = 482.3 (required 482.32).

Polymerization via the HWE reaction. Typical polymerization procedure was exemplified by the synthesis of polymer **8**: Monomer **E** (0.5680 g, 0.475 mmol) was dissolved in THF (5 ml) and NaH (0.0340 g, 1.42 mmol) was then added. A solution of compound **22** (0.1710 g, 0.451 mmol) and compound **3** (0.0110 g, 0.024 mmol) in THF (5 ml) was added into the above solution while stirring. The resulted mixture was refluxed for 4 hours and the red polymer started to precipitate out. The reaction was stopped and the mixture was poured into

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methanol. The polymer was collected by filtration and purified by extraction in a Soxhlet extractor with methanol for 24 h. It was then dried under a vacuum at 50 °C for 2 days (0.55 g, 91%).

Polymer 7. ^{1}H NMR (CDCl$_2$-CDCl$_2$, ppm): d 0.90 (b, 6H, -CH$_3$), 1.35 (b, 8H, -(CH$_2$)$_2$-), 1.50 (b, 4H, -CH$_2$-), 1.85 (b, 4H, -CH$_2$-), 4.05 (b, 4H, -OCH$_2$-), 7.10 (b, 4H, vinyl protons), 7.48 (b, 6H, aromatic protons). Anal. Calcs. for C$_{28}$H$_{36}$O$_2$: C, 83.17; H, 8.91. Anal. Calcd. for C$_{28}$H$_{36}$O$_2$: C, 83.17; H, 8.91. Found: C, 81.58; H, 8.84.

Polymer 8. Similar ^{1}H NMR spectrum as polymer **9** was obtained. Since the solubility of polymer **9** is much better than polymer **8** in CDCl$_3$, ^{1}H NMR data of polymer 11 was presented here.

Polymer 9. ^{1}H NMR (CDCl$_3$, ppm): δ 0.89 (b, 15H, -CH$_3$ in alkoxy); 1.25 (b 3H, -CH$_3$ on chromophore), 1.35 (m, 22H, methylene protons), 1.55 (b, 10H, methylene protons), 1.87(m, 10H, methylene protons), 3.04 (b, 3H, -SO$_2$CH$_3$), 3.55 (b, 2H, N-CH$_2$-CH$_3$), 3.80 (b, 2H, -CH$_2$-CH$_2$-N), 4.10 (b, 10H, -OCH$_2$- on alkoxy side chain), 4.22 (b, 2H, -OCH$_2$-CH$_2$N-), 5 broad peaks at 6.70, 7.15, 7.31, 7.48, 7.70 were observed which couldn't unambiguously assigned. Anal. Calcd for : C, 74.02; H, 6.89; Ru, 0.72. Found: C, 75.33; H, 8.24; Ru, 0.09.

Characterization. The ^{1}HNMR spectra were collected on a Varian 500-MHz FT NMR spectrometer. The FTIR spectra were recorded on a Nicole 20 SXB FTIR spectrometer. A Shimadzu UV-2401PC UV/vis spectrometer was used to record the UV/vis spectra. Thermal analyses were performed by using the DSC-10 and TGA-50 systems from TA Instruments under a nitrogen atmosphere. The melting points were obtained with open capillary tubes on a Mel-Tem apparatus without corrections. Elemental analyses were performed by Atlantic Microlab, Inc., except the ruthenium analyses, which were done by Galbraith Laboratories, Inc.. Molecular weights were measured with a Waters RI GPC system using polystyrene as the standards and THF as the eluent.

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The photoconductivity was studied by measuring the voltage across a 1 MΩ resistor resulting from a photocurrent running through the sample. A Diode laser (690 nm) with an intensity of 20 mW was used as the light source.[24]

Second-order NLO properties of poled polymeric films were characterized by second harmonic generation measurements. A mode-lock Nd:YAG laser (Continuum-PY 61 C-10, 10-Hz repetition rate) was used as the light source. The second harmonic of the fundamental wave (1064 nm) generated by the polymer sample was detected by a photomultiplier tube (PMT), then amplified and averaged in a boxcar integrator. To measure the temperature dependence of the second order nonlinearity, a polymer film was mounted to a heating stage. The transmitted SHG signal was monitored while the sample was heated up.

The linear electrooptic coefficient , r_{33}, of the poled polymer films was measured at 690 nm using a reflection method.[14] A Soleil-Babinet compensator was used to bias the DC intensity at its half maximum intensity. The phase retardation between the p and s waves was modulated by an external oscillating field. The modulation of the intensity amplitude was determined using a lock-in amplifier, which was then used to calculate the r_{33} value.

A two-beam coupling experiment was performed using a diode laser (690 nm, 25 mW, Laser Power Technology, 690-300) as the laser source. The laser beam (s-polarized) was split into two beams, which were intersected in the polymer film at a geometry reported before.[25] The transmitted intensities of the two beams were monitored by Lock-in amplifiers and collected by a computer.

To measure the phase shift of the refractive index grating over the intensiy interference pattern, a motor driven pizoelectric translator was used to move the sample along the grating vector. The transmitted intensity of the two beams were collected in the same way as the two beam coupling experiment.

B. Stepwise Synthesis of Substituted Oligo(phenylenevinylene) via an Orthogonal Approach

Organic molecules which possess long conjugated systems are of interest for their electro-optic properties.[1] In particular, poly(phenylene vinylene) (PPV) has attracted much attention as an emissive material for use in electrolumiscent devices.[2] Incorporation of a conjugated block into a diblock system will provide us with new forms of materials. These diblock systems are expected to undergo microphase separation leading to new forms of self-assembled nano-scale materials containing a conducting domain which will be interesting for the study of the quantum confinement effect. OPV molecules possessing well defined conjugation lengths and structures may also serve as model systems for understanding the relationships between bulk material properties and molecular structures in conducting polymers.

Scheme 9 shows our strategy in synthesizing these OPVs. The open ended OPV chain always has a handle for further growth or other modification. The key to the overall strategy is the synthesis of building block molecules, monomers **1** and **2**, both of which possess mutually complementary functional groups at their ends. Monomer 1 possesses an aldehyde at one end and a vinyl group at the other end. Monomer **2** possesses an iodo substituent at one end and a phosphonate ester group at the other end. The iodo terminus of monomer **2** can couple with the vinyl terminus of monomer **1** under the Heck reaction conditions. Similarly, the aldehyde terminus of monomer **1** can couple with the phosphonate terminus of monomer **2** via the Horner-Wadsworth-Emmons chemistry. The strategic placement of the functional groups on monomers **1** and **2** allows for sequential and alternating addition of these monomers to an OPV chain as shown in Scheme 9. In order to control the growth of the OPV chain, it is necessary to effectively block one terminus of the growing OPV chain which was successfully accomplished with compound **3**. Growth of the OPV chain commences with compound **3** and thereafter monomers **1** and **2** are added in a repetitive stepwise fashion as illustrated in Scheme 9. An alternative approach to the rapid stepwise synthesis of OPV molecules is to react two equivalents of monomer **1** with one

Scheme 9: Synthesis of OPV molecules.

Reaction Conditions: i. Pd(OAc)$_2$, P(o-tolyl)$_3$, NBu$_3$, DMF. ii. NaH/DME. R = C$_8$H$_{17}$.
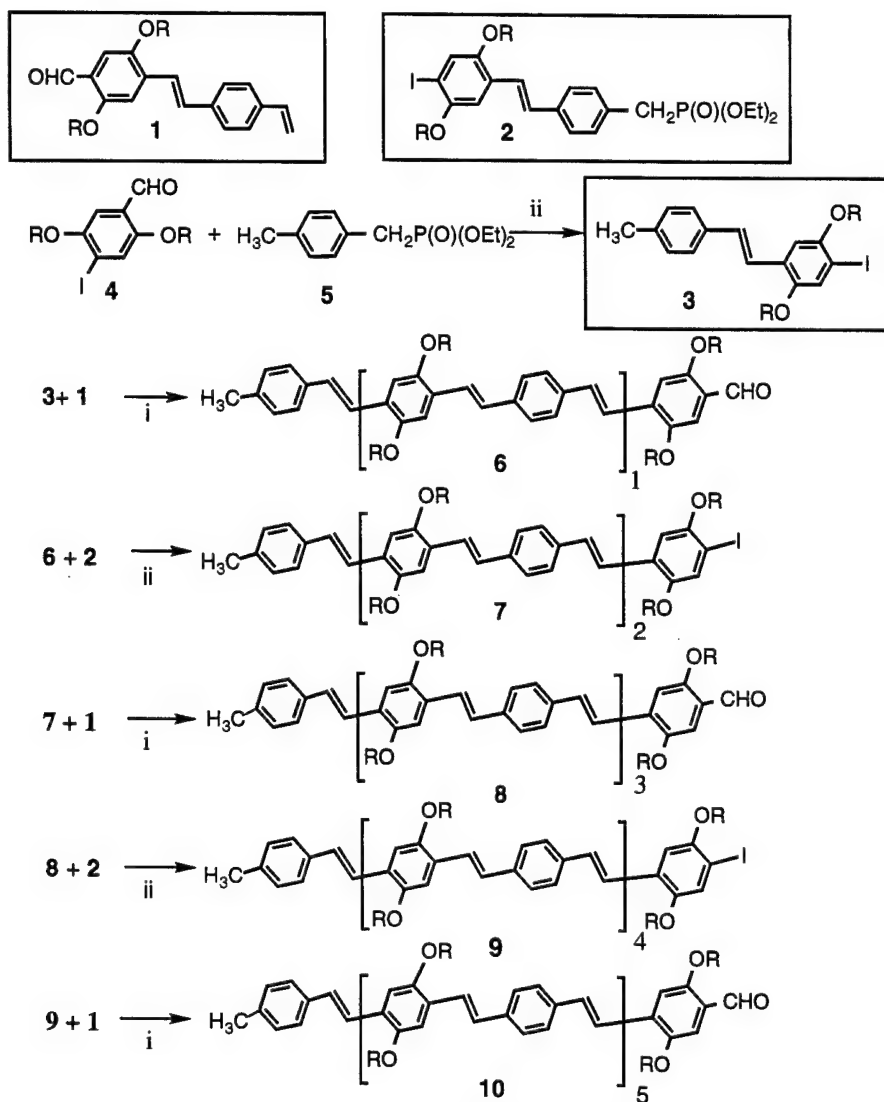
equivalent of 1,4-dibromobenzene. The product would have a conjugation length including 5 aryl rings and 4 double bonds, and in addition it would possess two aldehyde termini capable of reacting with two equivalents of monomer **2**. The process could be repeated to quickly build up longer OPV molecules possessing functionalized termini. Both monomers and compound **3** are

conveniently prepared from 4-iodo-2,5,-dioctoxy-benzaldehyde which is itself derived from 1,4-dihydroxybenzene in three simple steps.

The Horner-Wadsworth-Emmons reaction did give a detectable amount of the cis product (approx. 5%) as determined from ^{1}H NMR (chemical shifts in ppm). The Heck reaction also generates a small amount of regioisomers.[5] The minor double bond isomer from the Horner-Wadsworth-Emmons reaction and the Heck reaction could be separated from the product by flash column chromatography using a mixture of hexane and ethyl acetate as the mobile phase.[5] Interestingly, in the next Horner-Wadsworth-Emmons reaction to produce compound **9**, no cis product was detected. Reduced solubility of the longer oligomers poses a problem in the purification of these compounds, but analytically pure samples could be obtained through careful flash column chromatograph using mixtures of chloroform and hexane as the mobile phase. Yields for each of the steps are good to moderate with decreased solubility of the longer oligomers limiting the yields somewhat.[6] Presently, we have succeeded in the synthesis and purification of compound **10** which has 12 aryl rings, 11 double bonds in its conjugation pathway and a molecular weight of 2781. Synthesis of longer oligomers is still in progress. All of the spectroscopic studies and elemental analysis results are consistent with the proposed molecular structures.[7]

The absorption and emission spectra for the series of OPVs that possess an aldehyde end group are shown in Figure 4. All of the oligomers show strong and broad absorption in the visible region. Tripling the conjugation length from oligomer **4** to oligomer **8** results in a red shift of 32 nm. However, little or no red shift is noticed after the conjugation length reaches 8 aryl rings and 7 double bonds. The saturation in λ_{max} has been observed previously and arises because of the limitations to electron delocalization in the longer oligomers.[8] Thus the effective conjugation length in this series of oligomers is reached at compound **6**. The absorption wavelength maximum in the oligomers converges to that of PPV over relatively short conjugation lengths which suggests

the validity of using OPV to better understand the electronic properties of electroactive PPV materials.
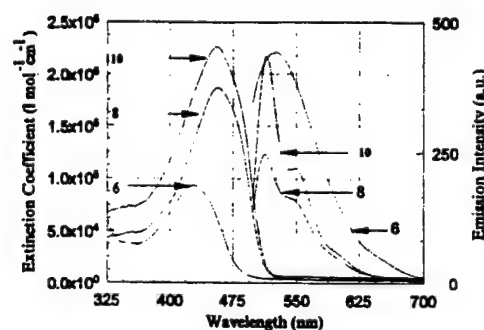

Figure 4. Absorption and emission spectra for compounds **6**, **8** and **10** taken in dilute solutions of choloroform.

Solutions of these oligomers give a brilliant green fluorescence (Figure 4). With the exception of oligomer **6** each of the oligomers exhibits three main features in their fluorescence spectrum in accord with theory.[9] There is a major band with a shoulder to the red of moderate intensity which is itself overlapped with a barely discernible weak band to the red. The emission spectrum of compound **6** is very broad and shows none of the fine structure present in the other spectra. The two main bands, discernible in other compounds, merged together in the fluorescence spectrum of compound **6** into a broad band with relatively higher intensity than the bands in each of the other oligomers. At present, it is not clear why this should be the case but it does appear to follow the general trend that in oligomers possessing aldehyde end groups the intensity of the second band grows as the conjugation length decreases. The fluorescence quantum yields of each of the oligomers is shown in Table I. No clear trend exists in the quantum yields but it is

interesting to note that the yields are substantially higher than the yields normally reported in PPV suggesting that defect sites and impurities act to reduce fluorescence quantum yields in conjugated polymers. No change in any of the emission spectra was observed when fluorescence measurements were made over a wide range of concentrations suggesting that excimer formation does not occur .

This series of all trans OPVs are rigid rod molecules and thus it is not too surprising that each of the oligomers, except compound **6**, manifests a reversible thermotropic liquid crystalline phase.[10] The melting temperature (T_m) and clearing temperature (T_c) for each oligomer is shown in Table I. These observations were made using polarized light microscopy to detect the mesoscopic state. The melting temperature and clearing temperature show a rough correlation with molecular weight. The temperature range over which the liquid crystalline phase persists gets broader with increasing conjugation length and the melting temperature gets higher as length increases in a series with the same end group. Figure 5 shows a micrograph of the liquid crystalline texture of compound **6**. The phase texture shows strong patterns characteristic of a nematic phase with a disclineation of 1.

Figure 5. Photograph of liquid crystal texture of compound **8** taken between crossed polarizers (magnification 200x (reproduced at 70% of original size), temperature 138 °C).

Table I. **Thermal transition temperatures and florescent quantum yield of OPVs**

Compound	6	7	8	9	10
T_m (°C)	97	67	90	113	105
T_C (°C)*	-	87	158	176	185
Φ_{fl} (%)**	75	87	81	89	82
λ_{max} (nm)	431	441	457	460	463

Note: * Clearing temperature from liquid crystalline phase to isotropic phase.

**: Excited at λ_{max}.

It should be pointed out that various syntheses of different OPVs have been reported in the past.[11-13] Schenk *et al* have investigated the charging capacity of OPV molecules and the charge distribution within the OPV chain.[11] Katz *et al* have studied the fluorescence dynamics of OPVs both in solution and the solid state and observed little difference between them.[12] The work presented in this report distinct from others in that our approach is open ended and very versatile, and it enables us to synthesize longer oligomers that more closely resemble organic polymeric conducting materials. Due to the fact that the Heck and Horner-Wadsworth-Emmons reactions tolerate a wide variety of functional groups, it should be possible to synthesize many different OPV molecules of various lengths and structures. This is useful for fine-tuning the band gap in emissive organic materials. Also noteworthy is the use of two reaction types to construct the same functionality, this eliminates the need of protecting groups. The use of a stilbene analog as the building blocks allows for efficient and fast construction of the OPV chain. After each step a functional group (either an aldehyde or iodo group) is left for further chemical manipulation which may include either continued elongation or reaction with an end functionalized polymer to form

novel diblock copolymers. Controlled bi-directional growth is also possible enabling a very rapid construction of OPV compounds possessing functional groups at both ends.

In summary, a general strategy for the stepwise synthesis of long conjugated molecules has been demonstrated. The strategy employs the use of two reaction types to grow the conjugated chain stepwise eliminating the need for protecting group chemistry. A similar strategy has recently been reported for the synthesis of dendritic molecules.[14] The molecules reported here showed high fluorescence quantum yields and a liquid crystalline phase. We intend to use these molecules in the production of novel diblock copolymers.

E. A Simple Orthogonal Approach To Phenylenevinylene Dendrimers

Dendrimers possess a multibranched structure that radiates out from a central core. The synthesis and characterization of these unique molecules have been the focus of attention of current polymer chemistry.[1] These molecules are not only aesthetically appealing but also possess some interesting physical properties, such as unusual glass transition behavior and viscosity and an isolating effect with certain functional molecules (e.g. porphyrin and rare earth ions).[2,3] A wide range of synthetic methodologies have been applied towards the efficient syntheses of dendritic macromolecules.[4] Two general approaches have been developed to synthesize these molecules: a divergent growth approach and a convergent growth approach.[5,6] For the synthesis of well-defined dendritic molecules, the convergent approach is preferred, as exemplified by the excellent works of Frechet, Moore and others.[7, 8] A general feature of these works is that the synthesis of each generation of dendrons involves the protection and deprotection of certain functional groups. Zimmerman disclosed an orthogonal approach in which aromatic moieties are alternatively linked by flexible ester linkage and rigid acetylene linkages.[9] However, this approach leads to the formation of dendrimers that are not homogeneous in chemical constituents due to the presence of different linkages.

Recently, we described an orthogonal approach for the synthesis of functionalized oligophenylenvinylenes in our diblock copolymer project.[10] In that approach two reactions, the

Heck and Horner-Wadsworth-Emmons reactions, were alternately utilized to construct a vinylene linkage. Due to the fact that both reactions mutually tolerate the functional groups involved, protection chemistry was not needed in each step of growth. A logical extension of this approach is to synthesize dendritic molecules bearing phenylenevinylene linkages. We designed two AB_2 type building molecules (**A** and **B**), one of which underwent the Horner-Wadsworth-Emmons reaction and the other underwent the Heck coupling reaction to produce higher generations of dendrimer bearing vinyl linkages. This strategy allows us to obtain homogeneous dendrons with a single functionality, which is either a bromo or formyl group, at the focal point.
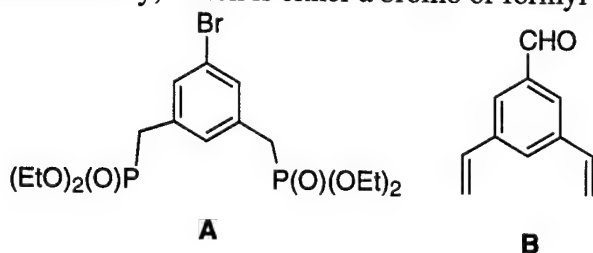
Benzylic bromination of 5-bromo-m-xylene followed by an Arbuzov reaction yielded compound **A**. Compound **B** was synthesized by monoformylation of 1,3,5-tribromobenzene followed by exchange of the remaining two bromide groups by vinyl groups via the Stille coupling reaction. Compound **A** reacted with 3,5-di-tert-butylbenzaaldehyde to obtain the first generation dendrimer, which was highly soluble in many common organic solvents such as $CHCl_3$, CH_2Cl_2, THF, toluene, etc (see Scheme 9). The higher generations were obtained by orthogonally using the Heck and Horner-Wadsworth-Emmons coupling reactions between the preceeding generation and the appropriate building molecules (see Scheme 10). The yield using the traditional Heck coupling conditions for the preparation of **G4** was poor.[11] However, higher yields (45%) were obtained using the protocol described by Meijere *et al* which uses K_2CO_3 as a base and tetra-n-butyl ammoniumbromide as a solid-liquid phase transfer catalyst.[12]

Scheme 10: Syntheses of dendritic molecules.
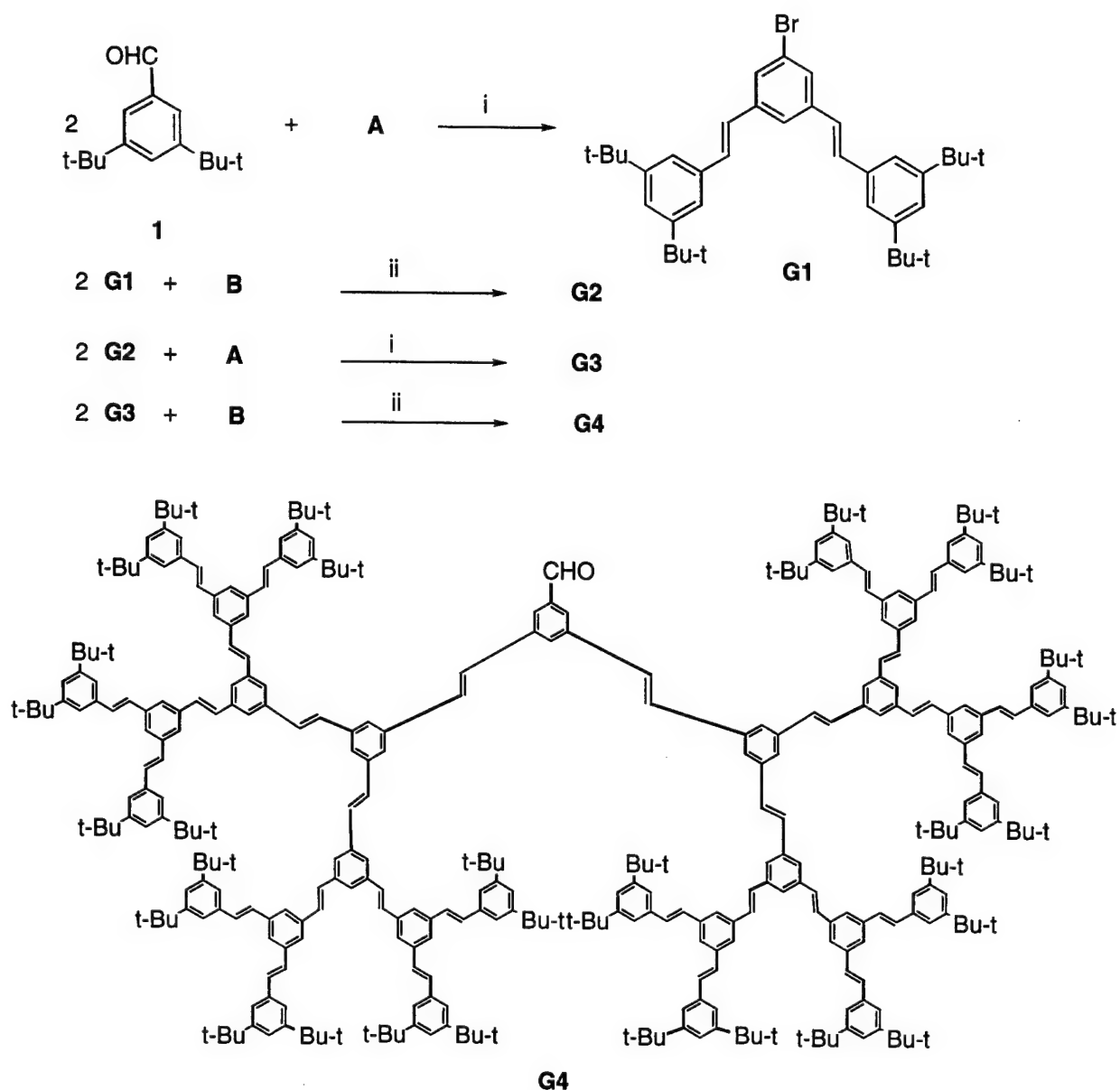
Reaction Conditions: i, NaH/NMP. ii, Pd(Ac)$_2$/N(n-Bu)$_4$Br/K$_2$CO$_3$

Since each generation of the dendrimers is functionalized at the central core, further chemical manipulation is possible. For example, a generation 3 dendron can be used to react with vinylbenzaldehyde to generate a molecule that has the aldehyde functional group with less steric hindrance (**G3.5**, Scheme 11). This molecule can then be used to couple with benzotriphosphate (compound **C**) to obtain a molecule with a higher molecular weight (compound **D**). Due to

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solubility problems, the yield of this coupling process is low (9%), but molecule **D** can be easily separated. It is a yellowish material with blue fluorescence. NMR and MALADI experiments have confirmed its structure.[13]

Scheme 11. Syntheses of **G3.5** and compound **D**.
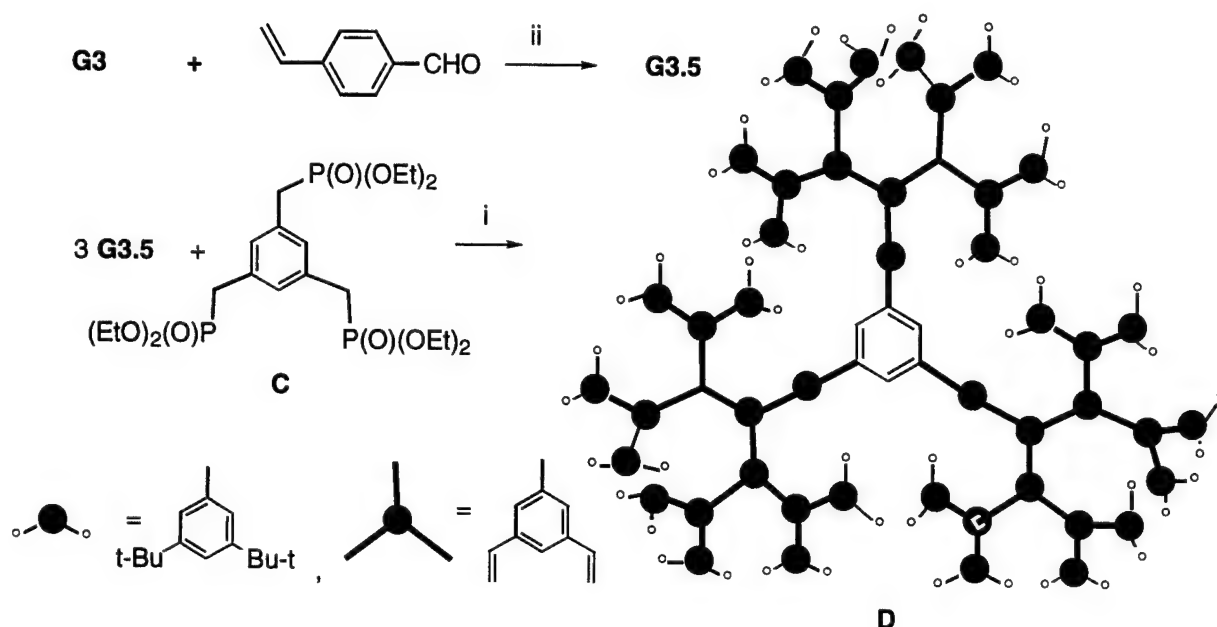
All of the dendrimers were characterized by using various analytical techniques. ^{1}H NMR spectra of the dentrimers become complicated when the generations become higher but the higher generations do possess the correct ratio of aliphatic to aromatic protons. Monosubstitution was ruled out because of the absence of a chemical shift caused by the terminal vinyl proton or benzylic proton in the purified dendrimer. Dendrimers **G2, G3.5** and **G4** all possess a proton chemical shift at about 10.15 ppm due to the formyl group. A chemical shift due to one of the vinyl protons can be identified as a doublet at about 7.2 ppm.

^{13}C NMR spectra of these dendrimers were very crowded in the 120 to 160 ppm region and it was difficult to assign every peaks. The aliphatic primary carbons and the tertiary carbons

associated with the t-butyl group appear around 32.5ppm and 35.9ppm, respectively, for all of the dendrimers. The four different carbons associated with the peripheral benzene unit with two t-butyl groups appeared around 152, 139.4, 123.3 and 121.9 in each case. The aldehyde carbon for **G2** and **G4** had a chemcal shift at 193 ppm.

Combustion results were in excellent agreement with the theoretical composition within the experimental error.[14] Firm evidence for the molecular structure was obtained from mass spectrometry results, using laser desorption ionization (MALADI). The mass spectra of all of the dendrimers showed the molecular ion peak at the calculated position.[13] Figure 6 exemplifies the mass spectrum of **G4**. It was found that **G3** and **G4** showed instability at the core vinyl linkage, as indicated by the occurrence of mass peaks at 1976 for **G3** (corresponding to the loss of **G1** less bromine) and 2556.5 (corresponding to the loss of **G3** less bromine).
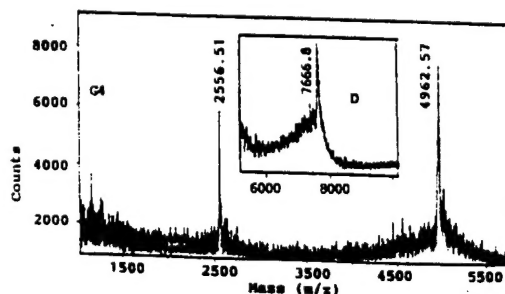

Figure 6. Mass spectrum (MALDI) of **G4**. The calculated molecular weight is 4965.6. The molecular ion peak for compound **D** is shown in inset. The theoretical value for that is 7673.8.

These molecules are almost colorless and the UV-vis spectrum of the **G1** dendrimer shows an absorption maxima at 306 nm (see Figure 7). A red shift was observed from **G1** to **G2-G4** and was caused by substitution effect. Dendrimers **G2** to **G4** exhibit virtually identical absorption maxima at 320 nm because these molecules contain cross-conjugation, implying that the major absorbing unit is stilbene in all the cases (the λ_{max} corresponding to the $\pi-\pi^*$ transition of

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stilbene is 294 nm). However, as the generations increase, the steric hindrance increases; the conjugation twists to different degrees from the periphery to the core. This effect is reflected by the fact that the extinction coefficient of **G4** is almost identical with that of **G3**. **G3.5** has a longer conjugation system at the aldehyde terminal and hence possesses a larger extinction coefficient.
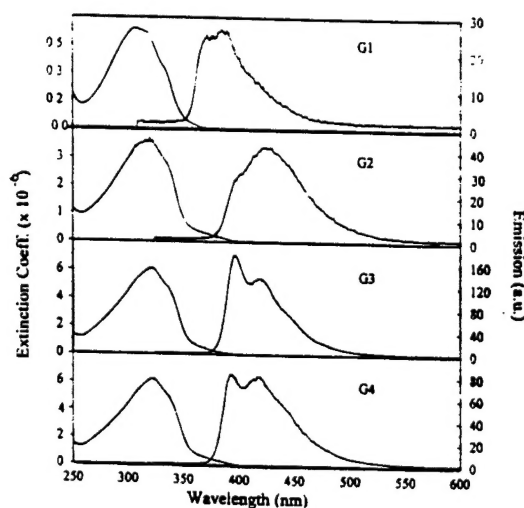

Figure 7. UV/vis and fluorescence spectra of G1-G4. The fluorescence spectra were taken from solutions having UV absorbance close to 0.2 AU and were normalized thereafter.

These macromolecules fluoresce in the the near UV (**G1**) or blue (**D2-G4**) region of the spectrum (see Figure 7). **G1** showed a low fluorescent quantum yield, probably due to effective quenching by the bromine atom. **G3** possesses a much higher quantum yield than **G1,** although it also contains a bromine group in the core position. **G2, G3.5** and **G4** all possess an aldehyde group at the core and they exhibited similar fluorescence spectra. Their fluorescence quantum yields increase as the generations increase.

G1 and G2 are crystalline materials with melting points at 150 °C and 350 °C , respectively. G3 and G4 did not show any thermal transition between room temperature and 500 °C as indicated by the DSC studies, both formed glassy materials.

We should point out that this work has several important points worth emphasizing. First, the synthetic approach developed here avoids the need for protection chemistry, which is needed almost exclusively in all dendrimer syntheses, except for the work by Zimmerman *et al*. The unique feature of this synthesis is that the orthogonal approach leads to the formation of a homogenous structure. This approach is also very versatile for the syntheses of different dendritic structures, which can be achieved through variation of the building molecules. The second point is that the dendrimers obtained contain π-electron systems which can be utilized to support charge carriers. The t-Butyl groups can be replaced with other functional groups, such as NLO chromophores. The functional group present at the focal point can be explored to add other functionality, such as a photosensitizer, to these molecules. Furthermore, higher dendritic molecules possess excellent film-forming properties. This is an ideal combination of properties for the design of dendritic photorefractive materials. Works along this line are in progress.

In conclusion, the strategy outlined here enables us to construct phenylenevinylene dendrimers with high molecular weights and without carrying out any protection-deprotection chemistries. The resulting dendrimers maintain the uniformity of the structure in terms of linking units involved between the generations. The reaction conditions are mild and simple, and can tolerate a large variety of functional groups. This approach will be applicable to build up other structurally uniform and well defined conjugated functional dendrimers.

CONCLUSION:

This AASERT grant is very useful in helping two of my domestic student in their scientific education and research. It gave them freedom to do creative research and offered them oppotunity

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to attend national meetings. Several important papers have been published based upon Todd Maddux's work. We think the effort suproted by this grant is very successful.